# Fire Risk and Hazard Analysis of Lithium-Ion Battery Technologies in Underground Facilities: A Literature Review

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**Report 5674, Lund 2022**

**Master Thesis in Fire Safety Engineering**

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Report 5674
ISRN: LUTVDG/TVBB—5674--SE

Number of pages: 103
Illustrations: 19

Keywords
lithium-ion battery, hazards, risks, thermal runaway, detection, fire protection

Abstract
The past decades have seen an exponential growth of the lithium-ion battery (LIB) market as use of this high-energy storage has found applications in nearly every industry. The European Organization for Nuclear Research (CERN) is interested in implementing this technology within their underground network and this literature review is intended to assist with addressing fire and safety concerns. This review is broken into four parts. Part I of this review introduces basic background information about LIBs, internal components, cell structure, cell chemistry, and a hierarchal understanding of different installation levels for LIBS. Part II of this review presents the fire risk and hazard analysis. The critical safety consideration when analyzing LIBs is prevention of a thermal runaway event. The sources of abuse that can cause a thermal runaway event (thermal, mechanical, and electrical abuse) are defined within this part of the report, as with the general internal decomposition stages as a LIB approaches thermal runaway. This focus on thermal runaway is important because at the point a LIB cell enters thermal runaway the internal heat generation within the compromised cell exceeds the cooling effects surrounding the compromised cell. An internal exothermic reaction can be a consequence from this unbalanced transfer of heat energy resulting in one or a combination of fire and safety hazards (i.e., toxic and flammable gas generation, fire, explosions, jet flames/flaming projectiles, electrical, and reignition). The factors that impact the severity and probability of each risk and hazard are also detailed in this part of the report to better address incident preparedness. Part III takes the fire risk and hazard analysis from part II, applies it to tunnel installations at CERN, and review current fire and hazard detection, prevention, mitigation, suppression, and extinguishing technologies. Key recommendations on implementation of the reviewed technologies within the CERN underground facility conclude this part. Part IV of this report begins with identifying current research gaps affecting this review and ends with the conclusion of the findings from this literature review.



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DEPARTMENT: FIRE SAFETY ENIGINEERING

Academic Year 2021-2022

**Fire Risk and Hazard Analysis of Lithium-Ion Battery Technologies in Underground Facilities: A Literature Review**

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Promoters: Prof. Patrick van Hees, Dr. Petra Andersson, & Dr. Oriol Rios

Master thesis submitted in the Erasmus Mundus Study Programme

**International Master of Science in Fire Safety Engineering**

## DISCLAIMER

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Read and approved,

Sean Meehan

June 8th, 2022

# Abstract

The past decades have seen an exponential growth of the lithium-ion battery (LIB) market as use of this high-energy storage has found applications in nearly every industry. The European Organization for Nuclear Research (CERN) is interested in implementing this technology within their underground network and this literature review is intended to assist with addressing fire and safety concerns. This review is broken into four parts. Part I of this review introduces basic background information about LIBs, internal components, cell structure, cell chemistry, and a hierarchal understanding of different installation levels for LIBS. Part II of this review presents the fire risk and hazard analysis. The critical safety consideration when analyzing LIBs is prevention of a thermal runaway event. The sources of abuse that can cause a thermal runaway event (thermal, mechanical, and electrical abuse) are defined within this part of the report, as with the general internal decomposition stages as an LIB approaches thermal runaway. This focus on thermal runaway is important because at the point an LIB cell enters thermal runaway the internal heat generation within the compromised cell exceeds the cooling effects surrounding the compromised cell. An internal exothermic reaction can be a consequence from this unbalanced transfer of heat energy resulting in one or a combination of fire and safety hazards (i.e., toxic and flammable gas generation, fire, explosions, jet flames/flaming projectiles, electrical, and reignition). The factors that impact the severity and probability of each risk and hazard are also detailed in this part of the report to better address incident preparedness. Part III takes the fire risk and hazard analysis from part II, applies it to tunnel installations at CERN, and review current fire and hazard detection, prevention, mitigation, suppression, and extinguishing technologies. Key recommendations on implementation of the reviewed technologies within the CERN underground facility conclude this part. Part IV of this report begins with identifying current research gaps affecting this review and ends with the conclusion of the findings from this literature review.

**Keywords:** lithium-ion battery, hazards, risks, thermal runaway, detection, fire protection

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# List of Acronyms

| | |
|---|---|
| AVD Agent | Aqueous Vermiculite Dispersion Agent |
| BESS | Battery Energy Storage System |
| BEV | Battery Electric Vehicle |
| BMS | Battery Management System |
| C&S | Codes and Standards |
| CCTV | Closed-caption TV |
| CERN | Conseil Européen pour la Recherche Nucléaire (EN: European Council for Nuclear Research) |
| CFRS | CERN Fire and Rescue Service |
| CID | Current Interrupter Device |
| DNVGL | Det Norske Veritas and Germanischer Lloyd |
| DoD | Depth of Discharge |
| ESS | Energy Storage System |
| Euro NCAP | European New Car Assessment Program |
| EV | Electric Vehicle |
| FAA | Federal Aviation Administration |
| FPRF | Fire Protection Research Foundation |
| FTIR | Fourier-transform Infrared Spectroscopy |
| GC-MS | Gas Chromatography – Mass Spectrometry |
| HAZMAT | Hazardous Material |
| HF | Hydrogen Fluoride |
| HRR | Heat Release Rate |
| HVAC | Heating Ventilation and Cooling |
| ICE | Internal Combustion Engine |
| IDLH | Immediate Danger to Life and Health |
| IR | Infrared |
| LCO Battery | Lithium Cobalt Oxide Battery |
| LFL | Lower Flammability Limit |
| LFP Battery | Lithium Iron Phosphate Battery |
| LIB | Lithium-ion Battery |
| LMO Battery | Lithium Manganese Oxide Battery |

| | |
|---|---|
| LTO Battery | Lithium Titanate Battery |
| NCA Battery | Lithium Nickel Cobalt Aluminum Oxide Battery |
| NFPA | National Fire Protection Association |
| NiCd Battery | Nickel Cadmium Battery |
| NMC Battery | Lithium Nickel Manganese Cobalt Oxide Battery |
| PCM | Phase Change Material |
| PCM | Protection Circuit Module |
| PHRR | Peak Heat Release Rate |
| PPE | Personal Protective Equipment |
| PTC Material | Positive Temperature Coefficient Material |
| SAE | Society of Automotive Engineers |
| SCBA | Self-contained Breathing Apparatus |
| SOC | State of Charge |
| SOH | State of Health |
| TMS | Thermal Management System |
| UNECE | United Nations Economic Commission for Europe |
| UV | Ultraviolet |
| VOC | Volatile Organic Compounds |
| VRLA Battery | Valve Regulated Lead Acid Battery |
| WA | Wetting Agent |

# 1. Introduction & Objectives

With the past decades of increased environmental research, human impact on the earth's climate has become a fact which we must accept. Caused by this reality, global powers have adopted an environmentally conscientious platform to address existing and projected climate change issues. Within the energy sector, popular solutions implemented to address these concerns is an increase of the use of renewable energy production sources (wind, solar, hydro, geothermal). This type of energy production, when both on and off-grid, is often integrated with lithium-ion secondary batteries (LIBs) to stabilize the power distribution in what is termed an energy storage system (ESS). A battery energy storage system (BESS) is an ESS that uses batteries as the medium for energy storage and LIB are just one of the possible battery types (Redox Flow, VRLA, Sodium-sulfer, etc.) used for a BESS. The LIB is a specific type of electro-chemical battery that has been around commercially since the 1990's [1] that has since taken over the majority share of the market for battery applications. This battery technology is found not only at the grand scale of a BESS but also found prolifically within the automotive industries increased production of electric vehicles (EVs) and at the local scale in many portable electronic devices. One only need to look around the room you are in, within your pockets, or at the device you are reading this report from to find an LIB powered device. This technology has been integrated deeply into modern living however there is still a gap in understanding the full picture of fire risks and hazards. As a hazard, LIBs deserve their own classification as they are a combination of electrical, flammable, explosive, toxic, and corrosive hazards in a neat little package. In addition to the compounded hazards, LIBs come in a variety of chemistries, types, and configurations which further complicate the task of creating a universal emergency response guideline.

## 1.1 Project Cooperation with CERN

Knowing the challenge ahead, The European Organization for Nuclear Research (CERN) is interested in implementing this technology within their underground network. This would mean considering general portable devices (personal devices, power packs, tool packs, etc.), lightweight personal electric vehicles (bikes, scooters, etc.), utility electric vehicles (fork trucks, scissor lifts, etc.), and stationary ESSs. Work needs to be done to assess the fire risks and hazards for this technology installed in an underground facility to prevent significant (1) risk exposure to personnel, (2) damage to neighboring property, (3) disruption to accelerator operations, and (4) surrounding environmental exposure.

## 1.2 Thesis Purpose and Objectives

Lithium-ion batteries have been implemented prolifically into nearly all industries and have a variety of test and installation standards created to apply to these hazards. The method used to accomplish this literature review is a review of practical fire testing (from cell level to installation level), LIB handling recommendations (from manufacturers, international codes and standards, fire research groups, etc.), and tunnel fire dynamics.

### 1.2.1 Purpose

The purpose of this thesis research is to:

*Analyze current collection of lithium-ion battery (LIB) fire research to provide (1) present fire risks and hazards of LIB technologies, (2) recommend fire detection options, (3) recommended fire mitigation and extinguishing options, and (4) research gaps in managing LIB fires*

### 1.2.2 Objectives

Specific objectives include:

**Objective 1:** Investigate lithium-ion battery general fire development, fire risks associated with hazard types, and common fire hazards. Consider internal, external, and ambient conditions impacting the fire development such as battery chemistry, configuration, technologies, and state.

**Objective 2:** Compare existing detection technologies for application with lithium-ion installations. This is meant to consider the detection technologies working principle, installation concerns, and effectiveness for hazard type.

**Objective 3:** Address the range of fire mitigation and extinguishing methods for lithium-ion battery fires. This hazard, as many others, lacks a universal solution guaranteeing extinguishment so common fire mitigation options must be reviewed. The scope of this fire response should consider technology integrated within the battery cell level, within the battery pack/rack level, and external response options.

**Objective 4:** Identify research gaps in managing lithium-ion battery fires within underground facilities like CERN.

## 1.3 Limitations and Delimitations

The following *limitations* apply to this thesis project:

1. A significant amount of fire testing has been done on lithium-ion battery technology. However, there exists a limited number of lithium-ion battery fire testing within underground and tunnel environments so some inductive predictions will need to be made on the impact to lithium-ion battery fire development.

2. Lithium-ion batteries come in a variety of chemistries and configurations which directly impact the fire development and fire effects. This broad range may limit the applicability of possible response methodologies and technologies.

3. The scope of protected lithium-ion battery installations ranges from single cell portable devices to thousand cell energy storage systems. Without installation level fire testing, forecasting the fire severity from smaller bench level fire testing may prove inappropriate.

4. Due to the rate of lithium-ion battery technology development, the historical fire test data collected may differ from the current battery present in lithium-ion devices and installations.

The following *delimitations* apply to this thesis project

1. Fire gas handling systems will not be addressed within this thesis. It is recommended, particularly for underground LIB installations, future work should be done to address concerns of ventilation sizing for significant volumes of vented fire gases, explosive risks during gas handling, filtering toxic gases from vented gases, impact of ventilation on LIB fire development, and stages of ventilation during LIB fire event.

2. There is no comparison between LIB codes and standards (C&S) or recommendations on standardization of LIB fire testing. Different abuse tests for LIBs are introduced by not elaborated on.

3. An explanation of the internal chemical reactions that occur within an LIB during thermal runaway is not detailed past the resulting vented gas species and their typical concentrations.

# 2. Methodology

The purpose of this thesis is to provide a fire risk and hazard analysis of LIBs, as well as address potential fire prevention, detection, and response strategies. A semi-systematic review or a narrative review approach has been utilized for this thesis to better prepare and present this topic. The flowchart summarizing the methodology used for this thesis [fig. 1] breaks down the project into 5 phases: intro, structure, collection, review, and writing.

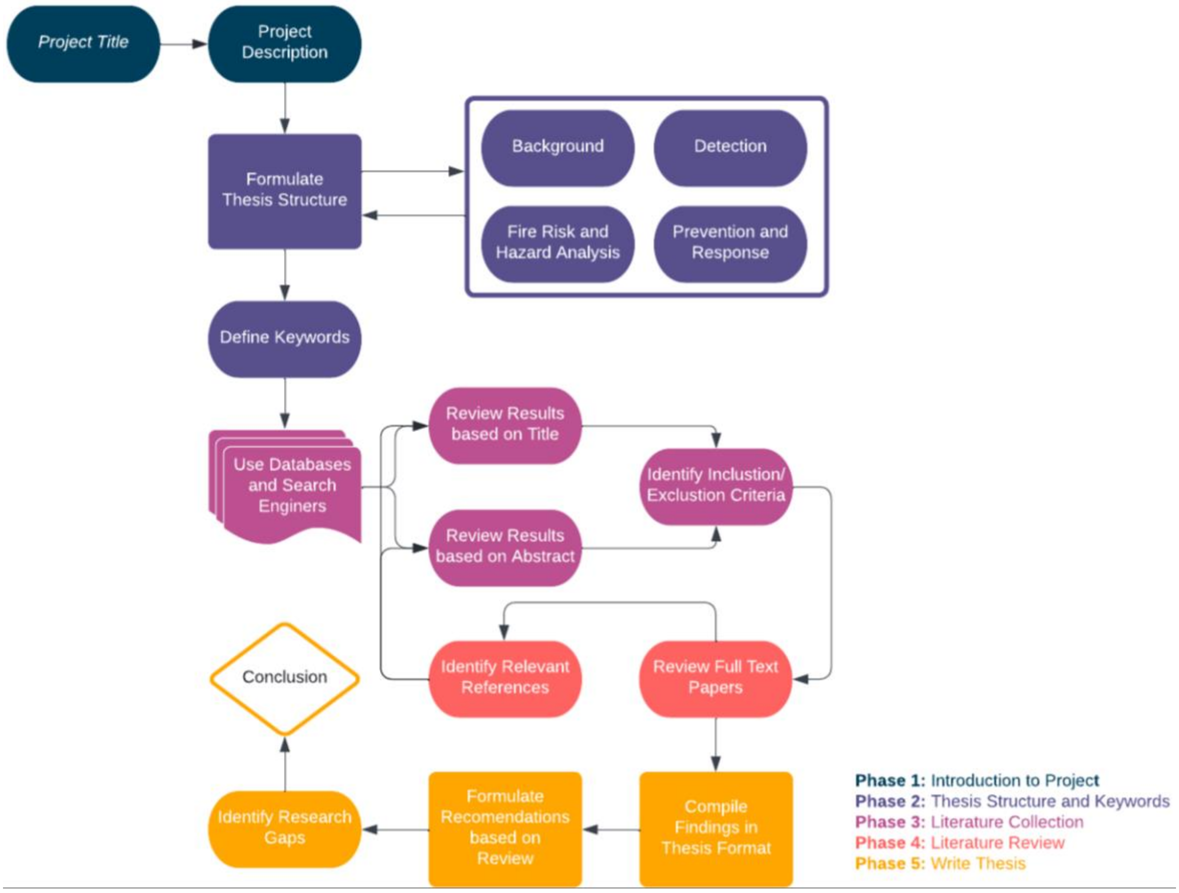



*Figure 1: Thesis Methodology Flowchart*

The introduction to the project (phase 1) consists of the preemptive meeting with the project supervisors to introduce the author to the project and organize a plan to complete the thesis within the allotted time. After the introduction, four initial references were provided by the supervisors. Of the four references, only two were used [2,3] to continue to the next phase. These introduced the general fire risks and hazards of LIBs and helped to formulate the thesis structure and define keywords (phase 2) when beginning the literature review. The literature review is split over two phases, phase 3 and 4. The first phase of the literature review (phase 3), is the collection and filtering of literature sources. This is done by using reputable search engines and databases, key search phrases, and a well-defined inclusion/exclusion criterion. At this basic filtering phase, the collected literature was sorted based on the literature's title or abstract. After this initial filtering, the full text was reviewed (phase 4) and relevant findings were recorded for the eventual final phase. Within phase 4, the applicable references found within the initial literature are collected to be filtered through phase 3 and its inclusion/exclusion criteria. The relevant findings collected in phase 4 is the base of the writing phase (phase 5) which is the final product you are reading now.

## 2.1 Keyword Definition

The keywords used to complete this literature review were chosen to be specific to the four main sections identified during the thesis structure formulation stage: background, fire risk and hazard analysis (FRHA), detection, and prevention and response. The following keywords listed below are usually preceded by the words "lithium-ion battery" to keep the focus of the search towards the topic.

**Background**: history, secondary batteries, applications, components, chemistries

**FRHA**: risks, hazards, fire testing, lower flammability limit, heat release rate, abuse sources

**Detection**: fire detection, early detection, gas monitoring, battery management system

**Prevention and Response**: prevention, suppression, extinguishment, firefighter operation

## 2.2 Database Search

The above noted keywords were used within several academic research databases: science direct, research gate, scopus, and google scholar. Science direct and scopus were the primary resource used to collect references but google scholar was very useful when collecting historical fire incidents involving LIBs.

## 2.3 Inclusion and Exclusion Criteria

The articles that have been found during the database search are collected and their titles or abstracts are read to be organized for further filtering. The further filtering stage is based on the inclusion and exclusion criteria. The search results are then narrowed by defining an exclusion and inclusion condition [table 1]. With each article read and new data obtained, this criterion is continually updated.

*Table 1: Inclusion and Exclusion Criteria for Thesis Methodology*

| Inclusion Criteria | Exclusion Criteria |
|---|---|
| Mention of LIB or underground within title or abstract | Standards for bulk storage of LIBs |
| Safety feature of LIB is being tested | Performance testing of LIB technologies |
| An experimental study involving fire testing of LIB | Enviornmental impact of LIB supply chain |
| Comparison of fire risks or hazards of LIBs | Detailed analysis of LIB electrolyte chemistry |
| Comparison between LIB and other secondary batteries | Detailed analysis of LIB components |
| Testing of detection, prevention, or response strategies with LIB hazards | Gas handling of LIB fire gases |

## 2.4 Full-text Review

The filtered literature serves as the foundation of the finding in chapters 3 to 9 of this thesis. Chapters 10 to 12 are recommendations, noted research gaps, and a conclusion based on the work presented in the preceding chapters. The filtered literature was subjected to meta-analysis and evaluation in accordance with the following guidelines:

- Overview of LIBs, including their different chemistries, construction, and capacities.
- Potential fire risks of LIBs and corresponding hazards.
- Fire detection options specific to LIB technologies
- Fire prevention and response options for failing LIB technologies
- Limitations and gaps of the existing LIB technologies and potential future testing

# PART I – Lithium-ion Battery Background

# 3. Brief History of the Rechargeable Battery

The first electrochemical battery was created by the Italian chemist and physicist Alessandro Volta in 1799 and was known as a "Voltaic Pile". This initial battery concept was crude in modern terms, but Volta's proof of concept began the electrochemical battery race to develop a battery with increased energy density, life span, and applications. An important division in the early development of electrochemical batteries is the difference between primary and secondary batteries. Primary batteries, like the Voltaic Pile, are one-use batteries that once constructed only discharge current until all the active material within the battery is spent. Then the battery must be disposed of and replaced with a new battery. This battery technology can often be found in modern devices such as digital watches, residential smoke detectors, and commercial remote controls. Secondary batteries, however, are rechargeable batteries that can cycle between charged and discharged for a specific lifetime thus improving the cost effectiveness of battery technology. This type of battery technology is found in all portable electric devices with a charging connection and is likely within the device you are using to read this thesis. The focus of this thesis is regarding secondary batteries, specifically lithium-ion battery technology. However, before plunging into the specifics of lithium-ion batteries as a secondary battery, a brief introduction to secondary batteries is necessary.

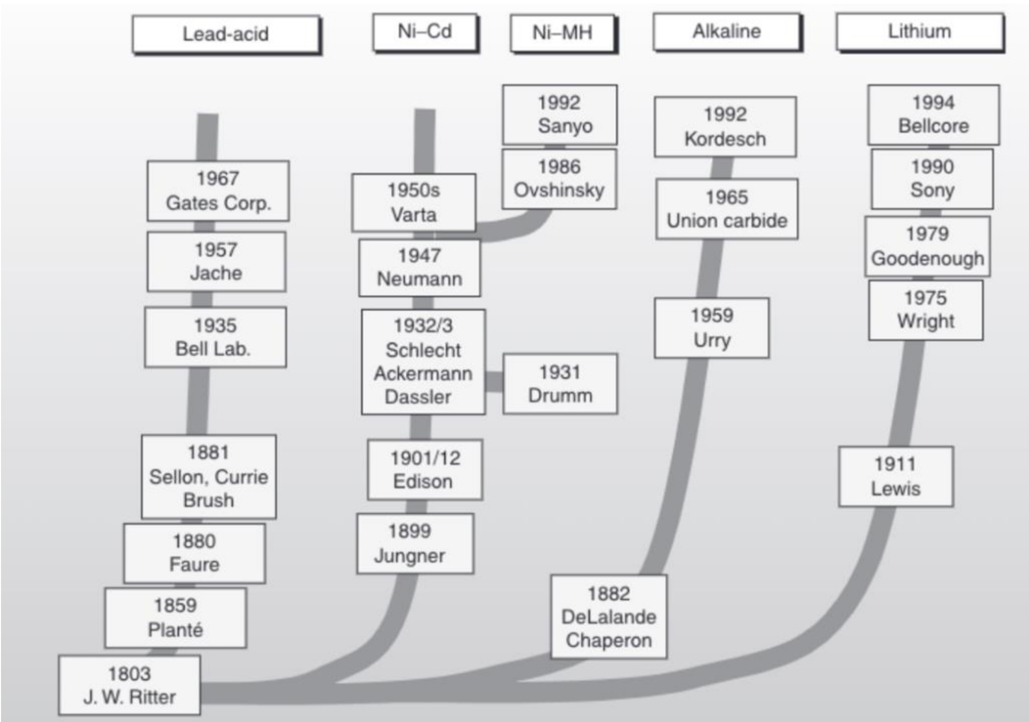



*Figure 2: Development of Secondary Battery Technologies* [4]

The first recognized secondary battery was created by the German physicist Johann Wilhelm Ritter in 1803 by layering disks of copper and cardboard soaked in a brine of table salt [4]. This battery (A.K.A. accumulators during this period) was referred to as the "Ritter Pile". Once the concept of a secondary battery became reality it found international support in major industries which supported competitive research and development. Figure 2 compiles the development of secondary battery technologies. From the over 200 years since the creation of the "Ritter Pile" a plethora of materials and designs have been tested in pursuit of a high energy capacity secondary battery with low operating costs. Of the secondary battery technologies created during this period the four commonly used secondary battery types are Lead-acid, Nickel-Cadmium, Nickle-metal-hydride, and Lithium-ion. Significant characteristics of these different secondary battery technologies are found in table 2. This table has been created by altering the original expanded table created by Battery University [5]. As shown in table 2, the LIB has significantly higher specific energy and cycle life, thus validating the improved performance of LIBs.

*Table 2: Characteristics of Commonly Used Secondary Batteries* [5]

| Specifications | Lead Acid | Ni-Cd | Ni-MH | Li-ion | | |
|---|---|---|---|---|---|---|
| | | | | Cobalt | Manganese | Phosphate |
| **Specific Energy [Wh/kg]** | 30 - 50 | 45 - 80 | 60 - 120 | 150 - 250 | 100 - 150 | 90 - 120 |
| **Internal Resistance** | Very Low | Very Low | Low | Moderate | Low | Very Low |
| **Cycle Life [80% DoD]** | 200 - 300 | 1000 | 300 - 500 | 500 - 1000 | 500 - 1000 | 1000 - 2000 |
| **Charge Time [hr]** | 8 - 16 | 1 - 2 | 2 - 4 | 2 - 4 | 1 -2 | 1 -2 |
| **Overcharge Tolerance** | High | Moderate | Low | Low. No trickle charge | | |
| **Self-Discharge/Month** | 5% | 20% | 30% | < 5%<br>Protection Circuit Consumes 3%/month | | |
| **Nominal Cell Voltage** | 2V | 1.2V | 1.2V | 3.6V | 3.7V | 3.2 - 3.3V |
| **Charge Cutoff Voltage** | 2.40 | Full Charge Detection by Voltage Signature | | 4.20<br>Some go to higher V | | 3.60 |
| **Discharge Cutoff Coltage** | 1.75V | 1.00V | | 2.50 - 3.00V | | |
| **Peak Load Current** | 5C | 20C | 5C | 2C | > 30V | > 30V |
| **Charge Temperature** | -20 to 50 °C<br>-4 to 122 °F | 0 to 45 °C<br>32 to 113 °F | | 0 to 45 °C<br>32 to 113 °F | | |
| **Discharge Temperature** | -20 to 50 °C<br>-4 to 122 °F | -20 to 65 °C<br>-4 to 149 °F | | -20 to 60 °C<br>-4 to 140 °F | | |
| **Mainenance Requirements** | 3 - 6 Months | Full Discharge every 90 days when in Full Use | | Maintenance-free | | |
| **Safety Requirements** | Thermally Stable | Thermally Stable, Fuse Protection | | Protection Circuit Mandatory | | |
| **In Use Since** | Late 1800s | 1950 | 1990 | 1991 | 1996 | 1999 |
| **Toxicity** | Very High | Very High | Low | Low | | |
| **Coulombic Efficiency** | ~ 90% | ~70% Slow Charge | | 99% | | |
| **Cost** | Low | Moderate | | High | | |

The current direction of research in secondary batteries has been directed towards lithium-ion battery technology due to the increased performance noted by the higher specific energy and cycle life. This increased performance propelled this type of battery into the transportation sector as powertrains for modern electric vehicles. Although the first electric car built back in 1832 was powered by lead-acid type batteries [6], the improved energy density of lithium-ion made the transition understandable. Schweber [7], investigated differences of both gravimetric and volumetric energy density of common batteries and gasoline. The recorded energy densities [table 3] highlight the jump to higher energy density LIBs have compared to other batteries. However, the current energy density of LIB are distances away from gasoline and likely other petroleum-based fuels. Additionally, since lithium is one of the most electropositive materials, a battery implementing this material will. demonstrate a higher positive charge average of 3.6 V compared to 1.2 – 2 V for other secondary battery technologies. The rate of secondary battery development has recently accelerated due to performance demands and decreasing costs [8,9].

*Table 3: Energy Densities of Common Automotive Powertrain Energy Sources* [7]

| Specification | Nickel Cadmium | Nickel Metal Hydride | Lead Acid | Lithium-ion | Gasoline |
|---|---|---|---|---|---|
| **Gravimetric Energy Density [Wh/kg]** | 45 - 80 | 60 - 120 | 30 - 50 | 100 - 160 | 12,200 |
| **Volumetric Energy Density [Wh/L]** | 120 | 240 | 30 - 50 | 350 - 450 | 9,700 |

The current direction of lithium-ion battery development is recognizing the flammability and volatility of their systems. Significant research is actively chasing the line between performance and safety [10]. Certain strategies being investigated have been compiled into this report on lithium-ion batteries which are discussed in detail in the following sections.

# 4. Lithium-ion Battery Construction

It is worth noting that the lithium-ion battery (LIB) mentioned in this report differ from the often-mistaken lithium metal battery. The working principle of LIBs is the electrochemical transfer of lithium ions from the positive electrode (cathode) to the negative electrode (anode) during the charging state and when lithium ions are released from the anode to return to the cathode the discharge state begins [11]. This transfer of lithium ions derives the name of LIBs and the differential of charges caused by the transfer generates stored energy potential that can result in the flow of electrons in the form of electricity. Additionally, LIBs do not contain lithium metal and thus does not include lithium's proclivity to violent reactions in the presence of water or other lithium metal fire risks. LIBs come in many shapes and styles and these different configurations can impact the overall performance, safety, cost, lifespan, specific power, and specific energy of the battery.

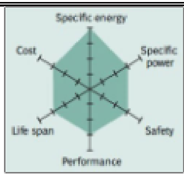
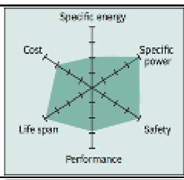
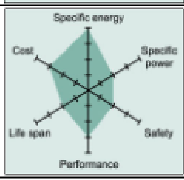
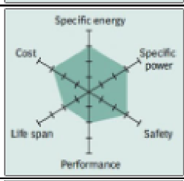
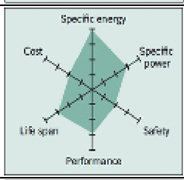
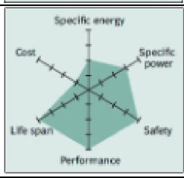
## 4.1 Components

LIBs are a secondary (rechargeable) electrochemical based battery known for their relatively high energy density, moderate lifespans, and a low self-discharge; particularly when compared to nickel cadmium (NiCd) or valve regulated lead acid (VRLA) batteries [5,12]. The LIB battery consists of four primary components: a positive electrode (cathode), negative electrode (anode), electrolyte, and separator. The separator is a necessary component to prevent the cathode and anode from physically touching (short-circuiting) but since it does not directly contribute to a fire event, it will not be addressed past its basic working principle. The separator will however be addressed further within the fire mitigation methods section 8.1.2. The other components (cathode, anode, and electrolyte) are mission critical and warrant a detailed explanation.

### 4.1.1 Cathode

The cathode or positive electrode is generally an aluminum substrate that is coated with a compound of an active material, conductive additive, and a binder. The composition of the cathode coating can vary depending on the manufacturer, but the working principle of the cathode is to control the capacity and voltage of the battery [13]. This control of capacity and voltage is defined by the ability of the cathode to store li-ions in a reaction called intercalation. Additionally, the chemistry of the cathode coating is generally the defining designation for the battery. The most common cathode coatings are lithium nickel magnesium cobalt (NMC), lithium iron phosphate (LFP), lithium cobalt oxide (LCO), lithium magnesium oxide (LMO), and lithium nickel cobalt aluminum (NCA). Each coating provides a benefits and critical criteria highlighted in table 4. The molecular structure of the coating can vary as well and the three common structures are layered oxide (LCO), polyanion (LFP), or spinel structure (LMO types), which all provide slightly varying performance benefits. For instance, cobalt-based cathodes form a tetrahedral layered oxide that allows 2-dimensional li-ion diffusion while manganese-based cathodes form a cubic crystal lattice system (spinel) that allows for 3-dimensional li-ion diffusion [17]. This difference in structure may have an impact on the thermal development at a molecular level but the intention is to focus on the macrolevel regarding associated fire risks and hazards.

*Table 4: Summary of LIB chemistry specific applications, critical characteristics, benefits, and drawbacks* [14–16]

| Chemistry | Applications | Critical Characteristics | | Benefits | Drawbacks |
|---|---|---|---|---|---|
| Lithium Nickel Manganese Cobalt Oxide (**NMC**) $LiNi_xMn_yCo_zO_2$ | Power Tools, E-Bikes and EV Powertrains, Medical Devices, General Industrial |  | Voltages: 3.0 - 4.2 V/cell<br>Capacity: 150 - 220 Wh/kg<br>Charge (C-rate): 0.7 - 1 C<br>Discharge (C-rate): 1 - 2 C<br>Cycle Life: 1000 - 2000<br>Thermal Runaway: 210°C (410°F)<br>Cost: ~$420/kWh | Adjustable performace criteria based on different ratios of Ni, Mn, and Co in the cathode. High thermal stability. High capacity and high power. | Limited to either a power build or energy build based on cathode ratios. Mechanically unstable. Relatviely lower voltage. |
| Lithium Iron Phosphate (**LFP**) $LiFePO_4$ | Portable and stationary devices needing high load currents and endurance. |  | Voltages: 2.5 - 3.65 V/cell<br>Capacity: 90 - 120 Wh/kg<br>Charge (C-rate): 1 C<br>Discharge (C-rate): 1 - 2.5 C<br>Cycle Life: 2000+<br>Thermal Runaway: 270°C (518°F)<br>Cost: ~$580/kWh | More tolerant to full charge conditions, less stressed than other LIBs at prolonged high voltage. High specific power, safety, and lifespan. Low cost. | Lower nominal voltage, specific energy, and energy density. Limited temperature range for performace criteria. |
| Lithium Cobalt Oxide (**LCO**) $LiCoO_2$ | Mobile Phones, Tablets, Laptops, Cameras, |  | Voltages: 3.0 - 4.2 V/cell<br>Capacity: 150 - 200 Wh/kg<br>Charge (C-rate): 0.7 - 1 C<br>Discharge (C-rate): 1 - 2.5 C<br>Cycle Life: 500 - 1000<br>Thermal Runaway: 150°C (302°F)<br>Cost: ~$420/kWh | High specific energy, low cost, long discharge period | Low thermal stability. Short lifespan. Limited load capabilities. |
| Lithium Manganese Oxide (**LMO**) $LiMn_2O_4$ | Power Tools, Medical Devices, Electric Powertrains |  | Voltages: 3.0 - 4.2 V/cell<br>Capacity: 100 - 150 Wh/kg<br>Charge (C-rate): 0.7 - 1 C<br>Discharge (C-rate): 1 C<br>Cycle Life: 300 - 700<br>Thermal Runaway: 250°C (482°F)<br>Cost: ~$420/kWh | Quick charge capabilities. Higher current. Better thermal stability. | Very short lifespan. Low performance. |
| Lithium Nickel Cobalt Aluminum Oxide (**NCA**) $LiNiCoAlO_2$ | Medical Devices, Electric Powertrains, General Industrial |  | Voltages: 3.0 - 4.2 V/cell<br>Capacity: 200 - 260 Wh/kg<br>Charge (C-rate): 0.7 C<br>Discharge (C-rate): 1 C<br>Cycle Life: 500<br>Thermal Runaway: 150°C (302°F)<br>Cost: ~$350/kWh | High specific energy. Low cost. Good specific power. Good for high-load applications. | Very low safety. EVs require monitoring for applications. |
| Lithium Titanate (**LCO**) $Li_4Ti_5O_{12}$ | UPS, Electric Powertrains, BESS, Aerospace |  | Voltages: 1.8 - 2.85 V/cell<br>Capacity: 50 - 80 Wh/kg<br>Charge (C-rate): 1 - 5 C<br>Discharge (C-rate): 10 C<br>Cycle Life: 3000 - 7000<br>Thermal Runaway: 210°C (410°F)<br>Cost: ~1,005/kWh | Very safe. Great thermal stability. Fast charging. High discharge current. No SEI film formation. | Very expensive. Low specific energy. Low intrinsic voltage. |

Since the cathode is often the defining aspect of an LIB, it is worth considering the market share of each battery type. A useful metric to look at is the automotive industry with their majority stake in the LIB industry. Projections presented at the 31st International Battery Seminar & Exhibit] show an increase in NMC type cells mass percent in LIB market shares [18]. NMC type cells are projected to increase from 26% in 2016 to 41%. In 2025

## 4.1.2 Anode

The anode or negative electrode is made from graphite or other carbon-based materials with minor exceptions. The primary material used for an anode is graphite, 90% of all LIB anodes are built on stable and affordable graphite [11]. The anode has the same working principle of the cathode in being able to store li-ions transferred between electrodes during charging or discharging states. Graphite is effective at intercalation with minimal expansion and comes with the bonus of being a cheap and abundant material. The other materials used for the anode are lithium titanate (LTO), hard carbon, tin/cobalt alloy, and silicon. Note. That LTO is the shown in table 4 as the sixth common LIB type due to its increase of industrial use and difference in performance criteria.

### 4.1.3 Electrolyte

The final component, the electrolyte, is a non-aqueous medium that allows only the movement of lithium ions. The electrolyte is generally composed of $LiPF_6$ salt for the passage of lithium ions, solvents to dissolve the salts, and select additives for improved efficiencies [13]. The movement speed of the lithium ions is dependent on the properties of the electrolyte and is thus important in the charging and discharging capabilities of the LIBs. The non-aqueous electrolyte that is used, is made of a combination of linear and cyclic alkyl carbonates [19]. Li et al. [20] lists the common organic carbonate solvents [table 5] and their distinct physiochemical properties. Regardless of the final electrolyte formula, lithium is used as the anodic active compound. This results in the high power and high energy density characteristics of LIBs. Conversely, with the improved performance comes high volatility and flammability caused by the organic based electrolyte which, sensitive to extreme temperatures and voltages, can generate significant gas and heat [14]. This liquid electrolyte is a critical aspect of LIB fire development and has been the focus of research to create a non-flammable electrolyte [20]. Some possible solutions include aqueous, ceramic solid, and polymer electrolytes along with ionic liquids and heavily fluorinated systems. For the present time we are primarily concerned with the prevalent non-aqueous flammable electrolyte. The data presented in this thesis considers primarily LIBs with $LiPF_6$ as the electrolyte.

*Table 5: Physiochemical Properties of Some Common Solvents* [20]

| Solvent | FW [-] | d @ 25°C [g/cm$^3$] | $\varepsilon_r$ @ 25°C [-] | $\eta$ @ 25°C [mPa] | $E_{homo}$ [eV] | $E_{lumo}$ [eV] | melting point [°C] | boiling point [°C] | flash point [°C] |
|---|---|---|---|---|---|---|---|---|---|
| Ethylene Carbonate (EC) | 88 | 1.32 | 90 | 1.9 | -12.86 | 1.51 | 36 | 238 | 143 |
| Propylene Carbonate (PC) | 102 | 1.2 | 65 | 2.5 | -12.72 | 1.52 | -49 | 242 | 138 |
| Dimethyl Carbonate (DMC) | 90 | 1.06 | 3.1 | 0.59 | -12.85 | 1.88 | 5 | 90 | 17 |
| Ethyl Methyl Carbonate (EMC) | 104 | 1.01 | 3 | 0.65 | -12.71 | 1.91 | -53 | 108 | 23 |
| Diethyl Carbonate (DEC) | 118 | 0.97 | 2.8 | 0.75 | -12.59 | 1.93 | -74 | 127 | 25 |

## 4.2 Cell Structure

The three main cell configurations for LIBs are cylinder, prismatic, and pouch [Fig. 3]. These battery cells, although different visually, have the same general components as previously identified: the cathode, anode, separator, and electrolyte. In addition to the similar interior materials, the exterior material is shared between battery types, namely a metal exterior case. The reason for a metal cell case is because during normal operation the LIB cell is pressurized when the electrolyte is added and requires a container to handle these pressures. This construction is distinctly different than the plastic cases used by lead acid batteries. To accommodate for the potential of over pressurization and prevent a mechanical explosion, a safety pressure relief is designed into the cell case to relieve over pressurization.

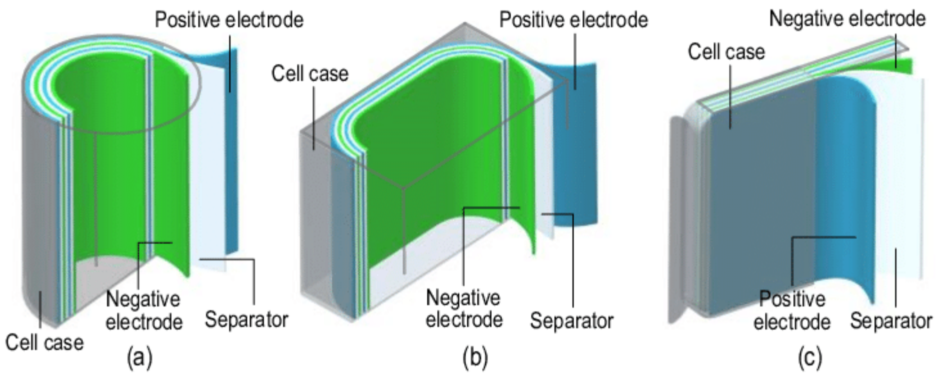



Figure 3: LIB Cell Formats (a) cylindrical, (b) prismatic, and (c) pouch [21]

## 4.3 Cell Chemistry

Whether the final completed cell is a cylinder, prismatic, or pouch type the key differentiation between LIBs is the composition of the electrode coating. Of the six most common LIB types [Table 3], five are termed based on the coating for the cathode (NMC, LFP, LCO, LMO, and NCA) while the remaining LIB type (LTO) is termed based on the coating for the anode. In Table 3, these 6 most common battery types are summarized to highlight their general applications of use, critical characteristics, benefits, and drawbacks.

## 4.4 Key Definitions for LIB Installations

To prevent confusion when reading this report, key definitions derived from UN 38.3 [22], UL 9540 [23], and UL 9540a [24] will be the prevailing terminology used throughout this report:

**Cell**: A single encased electrochemical unit (one positive and one negative electrode) which exhibits a voltage differential across its two terminals and may contain protective devices.

**Battery**: Two or more cells or batteries which are electrically connected and fitted with devices necessary for use, for example, case, terminals, marking or protective devices. Units which have two or more cells that are commonly referred to as “battery packs”, “modules” or “battery assemblies” having the primary function of providing a source of power to another piece of equipment.

**Component Cell**: A cell contained in a battery. A component cell is not to be considered a single cell battery.

**Lithium-ion Cell (LIC) or Battery (LIB):** A rechargeable electrochemical cell or battery in which the positive and negative electrodes are both intercalation compounds (intercalated lithium exists in an ionic or quasi-atomic form with the lattice of the electrode material) constructed with no metallic lithium in either electrode. A lithium polymer cell or battery that uses lithium-ion chemistries is regulated as a lithium-ion cell or battery.

**Single Cell Battery:** A cell externally fitted with devices necessary for use in equipment or another battery which it is designed to power, for example protective devices.

**Lithium-ion Battery (LIB) Module**: A single frame assembly comprised of interconnected LIB cells (e.g. 10-70 LIB cells) meant as a subassembly for an LIB pack or rack. The single frame assembly is meant to protect the cells from external shocks, heat, and vibrations.

**Lithium-ion Battery (LIB) Pack**: The final shape of an LIB system installed to an electric vehicle, A.K.A. LIB pack powertrain. Composed of multiple LIB modules (8-12 LIB modules per pack) and various control/protection systems including a battery management system (BMS), cooling system, and additional external shock, heat, and vibration protections.

**Lithium-ion Battery (LIB) Rack**: The final shape of an LIB system installed as a stationary energy storage system. Composed of multiple LIB modules (8-12 LIB modules per rack) and various control/protection systems including a battery management system (BMS), cooling and ventilation system, and fire protection systems.

**Battery Management System (BMS)**: A control unit integrated to maintain safe operation of the LIB unit. The BMS is intended to monitor LIB cell for abnormal conditions and present corrective measures such as electrical and thermal balancing

## 4.5 Hierarchy of Installations

In addition to differences in cell structure and chemistry, LIB technologies also vary in levels of installations, often termed capacity and quantified in watt-hours (Wh). The range of LIB installations range from single cell LIBs up to LIB systems made up of thousands of interconnected cells. The average range of capacities for LIB devices has been compiled by Euralarm [25] and paired the devices to the LIB installation level [table 6].

Table 6: *Capacities of Applications of LIB Devices* [25]

| ***LIB Level*** | ***Device*** | | ***Capacity of LIB*** |
|---|---|---|---|
| Cell Level | Cameras | | 2.5 - 9 Wh |
| | Mobile Phones / Smartphones | | 7 - 10 Wh |
| | Laptops / Tablets | | 15 - 27 Wh |
| | Power Tools | | 3.6 - 18 Wh |
| Module Level | Vitality Elecric Mobility | | 50 - 500 Wh |
| | Electric Bikes | | 500 - 1250 Wh |
| Pack Level | Elecric Vehicles | Fiat 500 | 24 - 42 kWh |
| | | Renault Zoe | 41 - 52 kWh |
| | | Tesla Model 3 | 55 - 75 kWh |
| | | VW ID.4 | 62 - 82 kWh |
| | | Ford Mach-E | 76 - 99 kWh |
| | | Porche Taycan | 79 - 93 kWh |
| | Electric Buses | | 100 - 500 kWh |
| | Electric Boats | | 20 - 200 kWh |
| Rack Level | Elecric Ships | | 200 - 2500 kWh |
| | Uninterruptable Power Supply | Small | 1 - 5 kWh |
| | | Medium | 50 - 100 kWh |
| | | Large | 100 - 200 kWh |
| | ESS | Residential | 5 - 50 kWh |
| | | Medium | 200 - 500 kWh |
| | | Large | 4000 kWh |

### 4.5.1 LIB Cell Level

The LIB cell level is the basic unit for LIB technology. At this level, the LIB cell consists of a single lithium-ion cell designed for use within equipment or another battery and equipped with limited protection and management devices. For example, a smartphone would fit into the LIB cell level category since it is powered by a single LIB cell and is supported by a basic battery management system (BMS) that can monitor the LIB temperature and basic electrical status such as state of charge (SOC) and state of health (SOH). At this level there is little to no consideration for thermal abuse or heat dissipation but often there is mechanical considerations to prevent physical abuse (vibration, shock, and penetration) to the battery cell. Standards and certifications at the LIB cell level [table 7] have been identified by Arora et al [26].

*Table 7: LIB Cell Related Standards and Certifications* [26]

| | US | International | Europe | China | Korea |
|---|---|---|---|---|---|
| **Certification/ Marks** | UL | IEC; IECEE | CE | CQC | KC |
| **Voluntary/ Mandatory** | Voluntary | Voluntary | Voluntary | Mandatory | Mandatory |
| **Factory Inspection** | Yes | Not required | Yes | Yes | Not required |
| **Certification Validity** | No expiration assuming no change in product | Contingent on standard upgrade | 10 years | As long as routine factory inspection is passed | No expiration, assuming no change in product |
| **Standards Applied** | UL 1642 | IEC 62133 | EN 62133 | GB 31241-2014 | Part 2, annex 05 of self-regulatory confirmation |

### 4.5.2 LIB Module Level

At the LIB module level, multiple cells (e.g., 10-70 LIB cells) are interconnected into a single frame that is meant to be a subassembly for an LIB pack or rack. The frame assembly is meant to further protect the batteries from external shocks, heat, and vibrations and depending on the manufacturer also consider cell-to-cell thermal propagation. In addition to the increased physical safety features, a more advanced BMS is integrated with the module to monitor thermal and electrical conditions for either the whole module or individual cells. Depending on the application for a battery module, a cooling system can be integrated to keep the LIB cells at working temperatures and dissipate heat introduced from ambient conditions and treatment status (charging and discharging).

### 4.5.3 LIB Pack/Powertrain Level

Interconnecting multiple LIB modules (e.g., 8 - 12 LIB modules) within a larger frame forms an LIB pack meant for an electric vehicle powertrain. The safety features of an LIB pack include advanced battery management system (BMS), cooling system, and an IP-rated enclosure to keep debris and moisture from interacting with the LIB modules. Additionally, increased safety concerns of EV LIB packs caused some auto manufacturers to impregnate the pack with insulating foam to both cushion the cells from shocks/vibrations and prevent internal and external thermal propagation. Standards and certifications at the LIB pack level [table 8] have been identified by Arora et al [26]. When seeking approval of an EV power train within the EU, Regulation No. 100 (R100) of the Economic Commission for Europe of the United Nations (UNECE) [27] provides a standard of provisions. Within the provisions the types of abuse testing for the LIB pack are defined. The abuse tests within R100 are vibration tests, thermal shock and cycling tests, mechanical shock, mechanical integrity, fire resistance, external short circuit protection, overcharge protection over-discharge protection, and over-temperature protection. These range of abuse testing provides a comprehensive understanding of the level of safety for the LIB pack.

*Table 8: LIB Pack Related Standards and Certifications* [26]

| | US | Canada | Germany | Japan | Russia | China | Korea |
|---|---|---|---|---|---|---|---|
| **Certification/ Marks** | UL | ULC | UL (DE), GS | DENAN | GOST | CQC | KC |
| **Voluntary/ Mandatory** | Voluntary | Voluntary | Voluntary | Mandatory | Mandatory | Mandatory | Mandatory |
| **Factory Inspection** | Yes | Yes | Yes | Not required | Yes | Yes | Not required |
| **Standards Applied** | IEC 60950-1 with UL 2054 | CSA 60950-1 with UL 2054 | EN 60950 and EN 62133 | DENAN Ordinance, Article 1, Appendix 9 | GOST 62133 | GB 31241-2014 | Part 2, annex 05 of self-regulatory confirmation |

### 4.5.4 LIB Rack/ESS Level

The LIB installation with the highest capacity is the LIB rack or LIB energy storage system (ESS) level. The LIB rack is like the LIB pack in that it is made up from interconnected LIB modules, but it is instead a stationary system with different safety considerations. To put this into perspective, EV LIB packs have capacities of roughly 25 – 100 kWh while LIB racks are greater than 200 kWh. The current largest LIB rack installation is the Moss Landing ESS that has a capacity up to 400 MW/1,600 MWh [28]. Other than the difference in capacities, LIB racks/ESS are installed in industrial rooms rather than IP-rated enclosures that allows more advanced safety devices. The advanced safety devices available at this level is state-of-the-art BMS, industrial HVAC systems, deflagration vents, fire detection network, and fire suppression systems

# PART II – LIB Fire Risk and Hazard Analysis

## 5. Lithium-ion Battery Fire Risks

LIB failures can result from thermal abuse [29–39], mechanical damage [30,32–34], electrical abuse [29,30,32–34,40,41], and manufacturing defects. These sources of abuse can, in certain instances, lead to a critical event known as thermal runaway [2,42–44]. When an LIB cell experiences a thermal runaway event, the cell experiences a series of exothermic reactions resulting in increasing internal pressure that leads to rupturing of the cell and release of toxic and flammable gases. Exposure and ignition to these released gases poses a significant safety and fire risk and a schematic [fig. 4] made by Wang et al. [45] shows the causes and basic effects of LIB failures. To better understand LIB fire risks, the sources of abuse will be detailed along with the critical concept of thermal runaway.

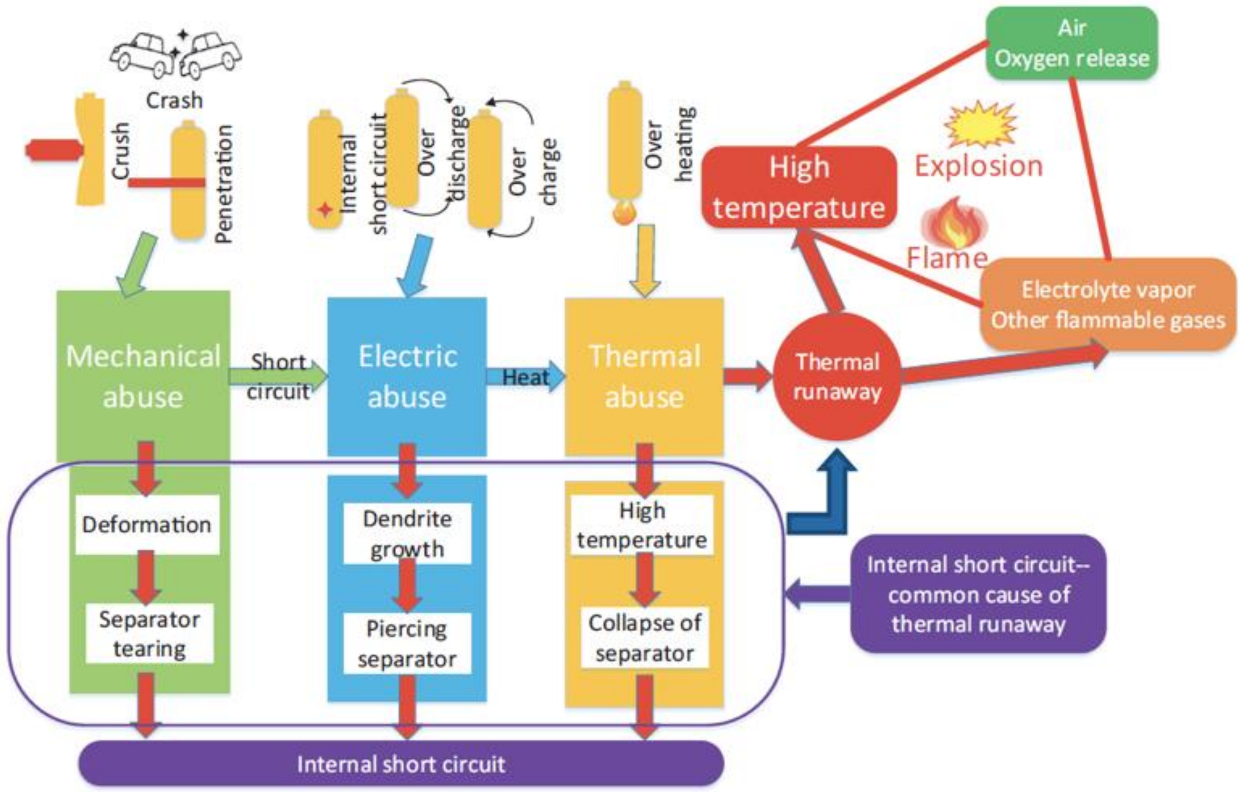



*Figure 4: Schematic of the Causes of LIB Fire Incidents* [45]

### 5.1 General Development of Thermal Runaway

In the case of a fire event for LIBs a critical phenomenon will occur known as thermal runaway, Thermal runaway is a process which has a different meaning depending on the specific discipline (chemical, electrical, civil, or nuclear engineering) using the term. Feng et al. [46] defined thermal runaway as the "state that occurs when the temperature of the LIB reaches a critical value…" while work done by Liu et al. [42] defined the process as "when the heat release rate from internal chain reactions are larger than the external cooling rate." The latter definition presented by Liu et al. better describes the process and focuses on the heat transfer conditions rather than a critical temperature. When an LIB cell experiences thermal runaway, the cell will rapidly enter a strong exothermic reaction producing significant volumes of flammable and toxic materials [44,47]. Therefore, if there is a significant heat dissipation capability within the battery module this fire hazard can be reduced. If the heat generated cannot be dissipated at a sufficient rate, then a fire event will likely occur. Two key factors that impact the probability of an LIB cell to enter thermal runaway is the cell's temperature and voltage. Each LIB cell has a defined safe window of operation that is between the manufacturer's specified temperature and voltage limits. Outside of these limits the probability of a thermal runaway event occurring increases. A helpful visual can be found from reading Bisschop et al. [48] which presents a "safety window". The premise is that the LIB cell should operate within a safe window between the minimum and maximum allowed voltage and temperatures. All to reduce the probability of a thermal runaway event.

To better understand the internal development of an LIB cell approaching and achieving thermal runaway experiments done with LIB cells heating using an external heater provided this road map [49]. Note that all mentioned temperatures are measurements made on the surface of the LIB cell.

1. The first component that degrades during an LIB fire event is the anode, this occurs at 80 °C.
2. The electrolyte breaks down and a gas is formed within the cell. This occurs at 100 – 120 °C and builds up a pressure within the cell. At a manufacture defined pressure, the safety relieve valve in the cell can operate to reduce the internal pressure.
3. At around 120 – 130 °C, the separator melts. This means the physical barrier between the anode and cathode fails and an internal short-circuit is possible. This would generate additional heat inside of the cell.
4. At around 130 – 150 °C, the cathode begins to degrade which, when using a metal oxide cathode, creates oxygen. Regardless of the generation of oxygen, this degradation is a highly exothermic reaction and produces a lot of heat.
5. At a cell surface temperature of 150 – 180 °C, the cell is in thermal runaway and the probability of propagation increases.
6. Past the occurrence of a thermal runaway event, the cell container can rupture and result in small explosions and/or fire spread.

Note that this cell thermal development is generalized, and the temperatures stated are not universal and can vary between installations. There are a variety of LIB chemistries, types, and configurations and therefore these temperatures should be taken with a grain of salt. Additionally, the true temperature that the internal event is occurring is different than the surface temperature of the LIB cell. This surface temperature generalization does however help direct thermal monitoring to better understand the state of the LIB cell. The thermal runaway event is critical when designing an LIB and Wang et al. [45] has shown that the common cause of thermal runaway is an internal short-circuit due to one or a combination of abuse sources. Investigation of internal short-circuits done by Santhanagopalan et al. [50] has identified four types of internal short-circuits for LIBs:

*Type 1*: a short between the two current collectors.
*Type 2*: a short between the negative current collector and cathode active material.
*Type 3*: a short between the positive current and anode active material.
*Type 4*: a short between the cathode and anode active materials.

These four types of internal short-circuits are presented in Bisschop et al. [48], and it should be noted that the material type specified for current collectors are typical for LIBs but not a universal truth for all LIBs.

Of the four types of internal short-circuits, type 3 has the highest probability of causing a thermal runaway event. This is caused by the relatively low electrical resistivity and onset temperature for self-heating reactions of the anode active material compared to the cathode active material. Type 1 internal short-circuit have been shown to raise the LIB cell surface temperature up to 100 °C [50] but due to the decent conductivity of the current collector, generated heat can be dissipated fast enough to prevent additional internal reactions. Type 2 has the lowest amount of localized heating compared to the other three. Type 4 is the most common types of internal short-circuits but the current flow is too low to be considered an immediate risk. That said all types of internal short-circuits can cause a thermal runaway event if the short is maintained over a long enough time.

## 5.2 Thermal Abuse

LIBs performance and safety has been shown to be negatively affected when operating at both low and high temperatures. At higher temperature conditions, caused either by high temperature environments or poor thermal dissipation, an internal degradation mechanism and exothermic reactions occur [48] which can result in a thermal runaway event [18,60,63] [43]. This is shown in the LIB cell thermal development roadmap from section 4.1. At lower operating temperatures, e.g., below 0 °C, the batteries internal resistance increases which promotes the growth of microstructures on the anode called dendrites. The formation of dendrites occurs over multiple charging cycles but if allowed to grow to the point of penetrating the separator an internal short circuit can occur within the battery [51]. This dendrite internal short circuit will cause heating effects within the battery and increases the likelihood of a battery fire [45,52,53]. Based on the importance of maintaining safe operating temperatures, the key questions to address when considering what type of LIB to install are: (1) What are the operating temperatures of the installation? (2) What are the LIBs listed safe operating temperatures? (3) What is the temperature the first LIB cell fails and enters the thermal runaway stage?

The first and second question are manageable, but the last question is not so cut and dry. The LIB cell chemistry, capacity, and treatment state also have an impact on the critical temperature that would send an LIB cell into thermal runaway. Regarding the differences between LIB cell chemistry, thermal runaway critical temperature for the six common LIB chemistries has been tabulated in table 3. Ouyang et al. [54] completed multiple tests on measuring impacts from increasing the number of batteries in an LIB installation, thus an increase of LIB capacity.  It was noted that an increase in LIB capacity increases the rate of temperature rise leading to quicker cracking of the battery cell safety relief. Quicker venting of the LIB cells accelerates the chance of forming a flammable or explosive environment before the vented effluent can naturally dissipate or be mechanically ventilated. The temperatures that the LIB cells failed remain the same regardless of the rate of temperature rise and capacity of the system. However, Ouyang et al. [54] also compared thermal abuse while the LIB undergoes one of the two battery treatments, charging and discharging, and it was identified that during the charging treatment the temperature that the LIB cells fail does decrease. This discovery would be indicative of the many fire incidents of EVs that have occurred while charging [55,56].

In response to the thermal sensitivity of LIB cells, codes and standards have been created to test an LIBs response to thermal abuse. One thermal abuse test is within UN 38.8 [22], where an LIB at 100% SOC is stored at 72 °C for 6 hours and then stored at -40 °C for another 6 hours. The metric of passing this test is that there is no leakage from the LIB cells and the SOC stays at or above 90% SOC. Other thermal abuse tests measuring both integrity and failure capacity of an LIB are found within UL9540 [23], UL9540a [24], UL1642 [57], SAND99-047 [58], SAE J2464 [59], and FreedomCAR [60]. The tests defined within the standards expose the LIB to various temperature ranges for specified durations to either simulate fire scenarios or monitor for impact on performance of the LIB.

## 5.3 Mechanical Abuse

The LIB cell is relatively fragile and only when fitted within an LIB arrangement does the LIB cell have some mechanical protection. If the LIB cell(s) are not protected and experiences significant mechanical abuse to cause either the cell casing to be penetrated or physically connect the electrodes, a resulting hazardous environment can form. Penetrating the cell casing will cause a leakage of flammable and conductive liquids while physically connecting the electrodes will form an internal short-circuit potentially leading to a thermal runaway event. An interesting factor impacting the likelihood of a thermal runaway event is the state of charge (SOC) during mechanical abuse. If an LIB has a lower SOC, there will be either a reduced or non-existent thermal runaway event [61]. Due to this risk, LIBs are bult into protective enclosures and even IP-rated enclosure particularly when installed into EV powertrains. If an LIB cell is mechanically abused enough to cause an internal-short circuit, the outcome will depend on the internal mechanical contact, heat generation, and electrical discharge [62]. All of which, if conditions allow, can lead to a thermal runaway event. EV LIB packs are built to withstand the greatest level of mechanical abuse but Zhu et al. [63] has still identified gaps in current physical protection designs for LIB packs.

In response to the relative fragility of LIB cells, testing codes and standards have been created to test an LIB and its protective enclosures response to mechanical abuse. Some such mechanical abuse tests are crush, impact, shock, vibration, or penetration tests. These different mechanical abuse tests are found specified within codes and standards such as UN 38.8 [22], UL9540 [23], UL9540a [24], UL1642 [57], SAND99-047 [58], SAE J2464 [59], and FreedomCAR [60].

## 5.4 Electrical Abuse

An electrical abuse to an LIB is generally caused by either excessive or prolonged current flow during a battery treatment state, both the discharge and charging states. Both treatment states cause internal chemical reactions which generate heat and if not dissipated can lead to overheating and over pressurization. The heat generated during the treatment state is called Joule heat and is generated whenever electrical current passed through a conduction material [48].

During the discharge treatment state, the flow of lithium-ions passes from the negative electrode to the positive electrode. Excessive current flow during discharge of an LIB can dissolve the negative current collector which will result in suspended conductive material within the electrolyte. The dissolved current collector increases the probability of an internal short-circuit and thus a thermal runaway event [64]. The other electrical risk during discharge is over discharge which occurs when an LIB discharges past its minimum voltage, 0% SOC. In significant cases when an LIB is discharged past complete discharge (0 V) the polarity of the cell reverses [65] and if allowed to continue can lead to significant damage to the internal cell components. Testing performed by Guo et al. [66] on NMC LIB cells identified three stages of failure during over discharge: (1) at -10% SOC the SEI layer on the anode begins to decompose, (2) at -12% SOC the negative current collector begins to dissolve, and (3) at charges below -12% SOC internal short-circuits begin to form with increased severity the lower the charge.

During the charging treatment state, the flow of lithium-ions passes from the positive electrode to the negative electrode. Excessive current flow during charging of an LIB can generate significant Joule heat within the cell and destabilize the cathode structure leading to lower decomposition temperature for the cathode [48]. These compounded risks significantly increase the risk of a thermal runaway event [67]. Testing the impact of excessive charging rates on LIBs has been independently done by several groups [67,68]. Both of which resulted in flaming or exploding LIB cells. The other electrical risk during charging is overcharging which occurs when an LIB charges past its maximum voltage, 100% SOC. When an LIB is charged past 100% SOC the electrodes can become significantly damaged. The anode will become overly lithiated past the point of lithium intercalation and form lithium metal on the surface in the form of internal short-circuit causing dendrites [64]. The cathode will do the opposite of the anode and instead become de-lithinated, causing the cathode material to decompose exothermically, generating heat [48]. Overcharging an LIB has been directly linked to self-heating mechanism which, if uninterrupted, can lead to thermal runaway. Test completed by Brand et al. [65] comparing LFP, NMC, and NCAN LIB cells and recorded self-heating mechanisms occurring at 105% SOC, 135% SOC, and 130% SOC respectively. This indicating LFP-based LIBs being least resistant to overcharge abuse. This can be concerning since fires caused by overcharge abuse are generally more vigorous and violent fires compared to LIB fires caused by thermal or mechanical abuse [69].

Mitigation options for electrical abuse are detailed in part III of the report but an important tool integrated in LIBs past the LIB cell level is a battery management system (BMS). The BMS is the “brain” of the battery and is meant to monitor for irregular electrical and thermal conditions and respond with an appropriate mitigation option (i.e. an integrated current break switch to prevent LIBs from exceeding the prescribed current limit or a temperature trip safety device) [43]. Most likely, an LIB fire incident caused by electrical abuse is due to the failure of the BMS [70].

Nevertheless, in response to the electrical abuse risks for LIBs, testing codes and standards have been created to test an LIB and it’s BMS response to electrical abuse. Some such electrical abuse tests are high-rate charge, high-rate discharge (external short circuit), overcharge, and undercharge tests.These different electrical abuse tests are found specified within codes and standards such as UN 38.8 [22], UL9540 [23], UL9540a [24], UL1642 [57], SAND99-047 [58], SAE J2464 [59], and FreedomCAR [60].

# 6. Lithium-ion Battery Fire Hazards

Once an LIB undergoes the critical event of thermal runaway, caused by one or a combination of abuse sources, a set of fire hazards begin to develop. LIBs are a unique risk due to the variety of potential fire hazards presented. Additionally, the severity and probability of these hazards have significant dependency on the LIB treatment state (charging or discharging) [54], over charging [71–73], state of charge (SOC) [74], ambient pressures [75], cell chemistries [76], and cell capacity [77]. The key fire hazards are addressed below which address all the variables which can impact the severity and probability.

## 6.1 Toxic and Flammable Gas Production

An early hazard generated during a thermal runaway event of an LIB is the ejection of toxic and flammable materials from the involved cells. These released materials can be either liquid or gas depending on the circumstances of the ejection but is referred to as effluent [22]. The liquid material ejected is of minor concern during a fire event whereas the gaseous products, contribute significantly to generating toxic and flammable conditions. The fire gases commonly generated when an LIB undergoes thermal runaway is characterized by the breakdown of alkyl carbonate electrolytes which produces a combination of organic and inorganic species, such as CO, CO2, $CH_4$, $C_2H_4$, $C_2H_6$, $C2H_5F$, $H_2$, and hydrogen fluoride (HF) [2,19,77–79]. Ignition of these gases within their range of flammability may result in fire and explosion scenarios. These scenarios pose a significant risk to surrounding life and property [2]. The challenge is that the species concentration of each gas is not universal for all LIBs and is impacted by several physical, electrical, chemical, and ambient conditions.

Of the species generated during LIB combustion hydrogen fluoride (HF) poses a significant toxic risk. Per US Department of Health and Human Services, the immediate danger to life of health (IDLH) value for hydrogen fluoride (HF) is the low exposure of 30 ppm (25 mg/$m^3$) [80] thus proving a significant concern due to the high toxicity at such low concentrations. Furthermore, HF poses a significant risk because the toxic gas can be absorbed through the skin as well as inhaled. However, the previously stated IDLH is referring to just inhalation exposure not the other two routes of exposure.

Fire tests comparing EV to ICE vehicles concluded that there is no need for additional safety measures for handling harmful fire gases like carbon-monoxide and hydrogen fluoride with standard firefighting personal protective equipment like a self-contained breathing apparatus (SCBA) and full turnout gear [81]. The reaction mechanism that forms HF is caused by the decomposition of the electrolyte salt LiFP6 in the following reactions.

$$\text{LiFP5} \rightarrow \text{LiF} + \text{PF5} \qquad (1)$$

$$\text{PF5} + \text{H2O} \rightarrow \text{LiF} + \text{POF3} + \text{2HF} \qquad (2)$$

$$\text{LiPF6} + \text{H2O} \rightarrow \text{LiF} + \text{POF3} + \text{2HF} \qquad (3)$$

Research completed by Kawamura et al. [82] and Wilken et al. [83] have identified that electrolyte salt reactions with moisture from contamination or external moisture further generates HF shown in chemical reactions 2 and 3. Wilken et al. [83] also concludes that the product of phosphoryl fluoride (POF3) will further react to moisture to form additional HF.

$$POF3 + H2O \rightarrow POF2(OH) + HF \quad (4)$$

FAAN LIB testing organized by Maloney and Rehn [77] tested a mixed group of LIB cell packaging and cell chemistries to highlight the average toxic fluoride emissions. The results were validated using two independent measurement techniques and recorded values of 20 – 200 mg/Wh of nominal battery energy capacity. Another toxic gas, POF3, measured 15-22 mg/Wh of nominal battery energy capacity. With the very low IDHL value for HF of 25 mg/m$^3$, significant concerns should be addressed when an LIB application is located within smaller enclosures. For perspective, if a 500 Wh LIB fire (rough value for an electric bike) occurred within a 300 m$^3$ enclosure the IDHL for HF will likely be exceeded as shown in equation 5.

$$500\, Wh\, LIB\ *\ 20\, mg\ of\ HF/Wh\, LIB\ \div\ 300\, m^3\ enclosure\ = 33.33\, mg\ of\ HF/m^3 \quad (5)$$

### 6.1.1 Electrical Impacts to Fire Gas Generation

Work done by Baird et al. [2] collected over 20 years of LIB fire testing with different cell chemistries, electrolytes, manufacturers, cell capacities, SOC, and failure modes. This work showed that as the state of charge (SOC) of involved cells increases, the species fraction of $H_2$ and CO increase and the $CO_2$ decreases. Key findings of Baird et al. work was:

- $H_2$ production increases about 20% for each cell chemistry above 40-50% SOC
- LCO cell fire testing shows at a SOC of 0-30%, less that 25% of fire gas volume is flammable. This changes dramatically at 40% SOC with an increase in flammable gas production and a decrease in $CO_2$ per volume.
- LFP cell fire testing shows less than 20% per volume of fire gas is flammable at 25% SOC. This increases to 30% per volume of flammable gases when the SOC increases to 50% and continues to rise with an increasing SOC.
- NCA cell fire testing has limited SOC tests at 0%, 50%, and 100% but trends show a significant hazard reduction at SOC below 40%

These findings were supported by the FAA study done by Maloney [77] which showed also at a higher SOC the battery electrolyte breaks down into smaller, more lightweight molecules that increase the total volume of gas emitted from the cells. Free burning tests organized by Willstrand et al. [84], showed a good linear relationship between HF production and nominal electrical energy for cell, module, and pack tests.

### 6.1.2 Chemical Impacts to Fire Gas Generation

Work done by Roth [85], has shown that the composition and volume of fire gases are connected to the chemistry of the electrolyte mixture and cathode. Compared to a collection of fire testing collected by Baird et al. [2], the total fraction of hydrocarbons in fire gas for

NCA and LFP LIB cells is 10-15% while LCO LIB cells had a fraction of 20-25%. The range concentrations of hydrocarbon in LIB fire gas have been noted by studies done by Lammer et al. [37] who tested LIB cells from different manufacturers with the same cathode chemistry and they produced different vent gas compositions. This variation may be due to differences in cell manufacturing but should be considered when predicting species concentrations in LIB fire gas.

### 6.1.3 Physical Impact on Fire Gas Generation

What about scalability? Due to financial and environmental reasons, lab and bench scale testing is the primary avenue for fire testing LIB technology. Ouyang et al. [54] has shown from review of a wide range of LIB fire tests that small-scale tests underestimated the gas concentrations of large-scale tests. It was predicted that the difference may be due to the increased peak temperatures reached, in turn caused by the increased number of LIB cells in the arrangement and additional physical configurations that shorten the propagation time between LIB cells. Although the under predicted gas concentrations in large-scale tests is concerning, fire testing comparing EVs to ICE in underground garages [84] showed no increased egress risk for the public. This highlights a translatable predictor for fire development and egress calculations for EVs in underground facilities.

### 6.1.4 Ambient Conditions

LIB testing done in inert environments can help measure the total production of gases in the absence of flame and is useful for comparative studies between different cell chemistries. Testing within inert atmosphere of LFP, NMC, and LMO cells completed by Sturk et al. [78] measured the volume of gas production normalized to the battery weight, rate of emission, and specific gas concentrations. The testing setup consisted of placing a battery consisting of five cells on a heated plate within an inert environment. One exterior cell is heated with the plate until achieving thermal runaway then the battery fire is allowed to propagate to the other four cells. The tests concluded the gas released, normalized to the battery weight the LFP battery 20 magnitudes less than the other chemistries. As for the measured emission rate of fire gases, the NMC and LMO batteries emitted at a. rate 100 times higher than the LFP battery. The difference in emission rates highlights the delayed propagation between LFP cells compared to NMC and LMO cells. HF emissions was measured using both a wash bottle and FTIR spectrometer which recorded comparable HF released between battery chemistries. However, since the volume of gases produced varies between battery chemistries, the LFP battery has a higher concentration of HF of the total released gases. In addition to the FTIR spectrometer a gas chromatography – mass spectrometry (GC-MS) analysis was done with the collected gas emissions. This analysis identified low volumes of acidic gases such as HF, HCl, and HCN that deserve consideration due to the low toxicity thresholds of these gases [86]. Overall, from testing done by Sturk et al. [78] shows that NMC and LMO-based technologies to be significantly more reactive than LFP-based technologies. An important caveat to note from LIB abuse testing in inert environments is the direct impact the inert atmosphere has on the formation of gaseous species. It is possible that chemical species measured are allowed to form within an inert environment that would be unstable in normal atmospheric conditions.

## 6.2 Heat Release

AN LIB undergoing thermal runaway experiences a self-heating mechanism that, if let alone, can result in significant releases of energy in the form heat. This often manifests as flaming combustion of the vented flammable gases from the failed LIB cell. Efforts made to understand the scale of heat generated by a failed LIB has not been easy with the complex and varying factors affecting the severity (i.e. LIB chemistry, SOC, capacity, and failure cause) [48]. This section addresses how these factors directly impact heat release of a failed LIB.

### 6.2.1 Cell Chemistry Factors

An important consideration regarding LIB fire safety is the term thermal stability. Bisschop et al. [48] defines thermal stability as the amount of heat generated per unit time when exothermic reactions have been triggered and is therefore a measure of safety regardless of the temperature the reactions would be triggered. From this definition, a material with a higher level of thermal stability the safer it is. Doughty et al. [87] reviewed the thermal stability of common cathode materials and ranked them as LFP > LMO > NMC > NAC > LCO with LFP being the most thermally stable. Additionally, Diaz et al. [88] have concluded that an LIBs heat of combustion is directly connected to its thermal stability. However, thermal stability is only one factor impacting the heat of combustion (i.e. LIB chemistry, SOC, capacity, and cell packing) [43,44,46].

Key qualities to quantify the severity of a fire event are the heat release rate (HRR), peak heat release rate (PHRR), growth rate, and radiative heat flux. It has been shown that these qualities are also impacted by the chemistry of the LIB. Ditch et al. [89] tested both LFP and LCO/LMO LIBs of similar electrical ratings and identified a significantly higher HRR and PHRR for the LCO/LMO LIB compared to the LFP LIB. The measured difference between PHRR between the LIBs with different cathodes was by a magnitude of three. This difference was also investigated by Xiang et al.  [90] who tested LIBs using LFP, LCO, and LMO cathodes and found that LIBs with LFP cathodes inhibit the decomposition of electrolyte. They measured reaction heats and onset temperature for decomposition reactions between LIBs with LFP, LCO, and LMO cathodes and just the electrolyte when heated from 20 °C to 220 °C. The respective results was 35 J/g with an onset at 218 °C, 358 J/g with an onset at 168 °C, 308 J/g with an onset at 110 °C, and in 258 J/g with an onset at 202 °C. These findings were supported by Brand et al. [65] who tested LFP, NMC, and NCA cells heated at a rate of 5 ºC/min and recorded onset temperatures of 212 °C, 212 °C, and 168 °C, respectively. Based on these tests, LIBs with LFP cathodes have better fire resistance qualities when exposed to elevated temperatures but Larsson [61] acknowledges the increased quantity of vented toxic and flammable gases which poses a different kind of risk.

### 6.2.2 Cell SOC Factors

Fire testing of LIB cells at different SOC has provided interesting differences in the HRR, PHRR, and thermal runaway onset temperature. Sturk et al. [91] tested LFP and NMC cells at 0V, 25% SOC, 50% SOC, 75% SOC, and 100% SOC and found that the total electrical energy content of an LIB cell is inversely related to activation energy for a thermal runaway event. A higher SOC for an LIB means less energy input is required to send an LIB cell into thermal runaway. AN LIB with a higher SOC goes through the stages leading to thermal runaway much quicker and in turn has a quicker HRR and often a higher PHRR. However, for LIBs with the same chemistry the total energy released is generally the same, regardless of the SOC during a thermal runaway event. These same conclusions have been independently found in agreement from testing by Larsson et al. [70,92], Ouyang et al. [71], and Golubkov et al. [74]. The tests done by Golubkov et al also noted that a minimum charge level was needed to initiate thermal runaway [74]. They heated LIBs with LFP and NCA cathodes to 250 °C at different SOCs to determine minimum charge level and the onset temperature for thermal runaway. The minimum charge levels were at least 50% SOC for LFP cells and 25% SOC for NCA cells. Additional tests at 100% SOC and 143% SOC showed significant self-heating at higher SOC noted by onset temperatures of thermal runaway at 140 °C and 65 °C, respectively. The increase in HRR for LIBs at a higher SOC can be accounted for by the increased lithiation of the anode which is more thermally sensitive and makes the anode highly reactive [50,74]. Additionally, it has been shown that increased oxygen generation occurs at higher SOC further increasing the severity of LIB fires at elevated charges [93]. Ouyang et al. [71] measured the radiative heat flux during their testing of NMC and LFP LIB cells and found a significant increase at higher SOC which further justifies the increased severity of LIB fires. A higher radiative heat flux translates to an increased rate of thermal propagation to neighboring cells compounding the number of cells actively contributing to the fire.

### 6.2.3 LIB Capacity Factors

The capacity of an LIB installation, often measured in Wh, refers to the maximum amount of energy available to store and distribute. The capacity of an LIB installation can be increased by either increasing the total number of cells or use LIB cells with higher individual capacities. Increasing the number of cells has direct implications to fire and heat generation risks that should be considered. Ouyang et al. [54] showed that increasing the number of cells within an LIB will increase the systems mass loss rate, peak heat flux, and radiative heat flux. The total mass loss rate may increase with an increase in the number of cells in the LIB but the mass loss rates of the individual cells does not change with the increased number of cells. A good source of quantifying the implications increased LIB capacity has on fire and heat generation are fire tests of LIB packs or EV powertrains. Fire testing completed to compare an EVs to an internal combustion engine (ICE) vehicle [43,44,81,91,94,95] have concluded a similar heat release throughout the duration of the fire except for the peak heat release rate (PHRR) which the EV can exceed, particularly when the EV is a pure battery electric vehicle

(BEV). This is comparison between ICEVs and EVs helps put the fire hazard of LIBs into perspective but comparing the test measurements with respect to the individual EVs capacities may help predict the severity of a fire based on capacity. Sun et al. [43,44] did just that and reviewed these and other fire tests on EV LIB packs and derived the equation:

$$PHRR = 2E_B^{0.6} \quad (6)$$

Where $E_B$ is capacity in Wh. This equation may not be the holy grail of fire risk assessments for LIBs, but it is promising. More testing needs to be done to confirm this for heavy industry EVs as seen for mining machinery and if this would be applicable for stationary LIB systems. At the bench-scale level, Ditch et al. [89] has tested the types of LIB cells commonly used for EV powertrains, LPF and LNO/LMO. Important correlations derived from their tests was the relationship between LIB capacity and both the total convective energy and maximum convective HRR [fig. 5]. The correlation between LIB capacity and the total convective energy was a found to be the same for both LIB cell types as a linear increase of 35.1 MJ/kWh of capacity. This linear correlation was also found by Willstrand et al. [84] under that assumption of a good oxygen supply. The correlation between LIB capacity and maximum convective HRR, a key criterion in quantifying the severity of a fire incident, was however neither linear nor synonymous between the LIB cell types. The function of maximum convective HRR to LIB capacity was non-linear with a predicted square function significantly increasing as the capacity increases. The plots and functions for both the LFP and LNO/LMO LIB cells are shown in figure 5. The non-linear increase is believed to be due to the extensive internal heating that occurs with larger LIB installations decreasing the time for onset of thermal runaway [89]. Based on the plot for maximum convective HRR the LFP measured significantly lower and would presents a lesser fire hazard than the LNO/LMO LIB cells. These bench-scale testing correlations are much less complex than the full-scale installations, LIB pack or rack, and thus extrapolating the data past the bench-scale is not recommended without better understandings of this complex burning behavior [89].

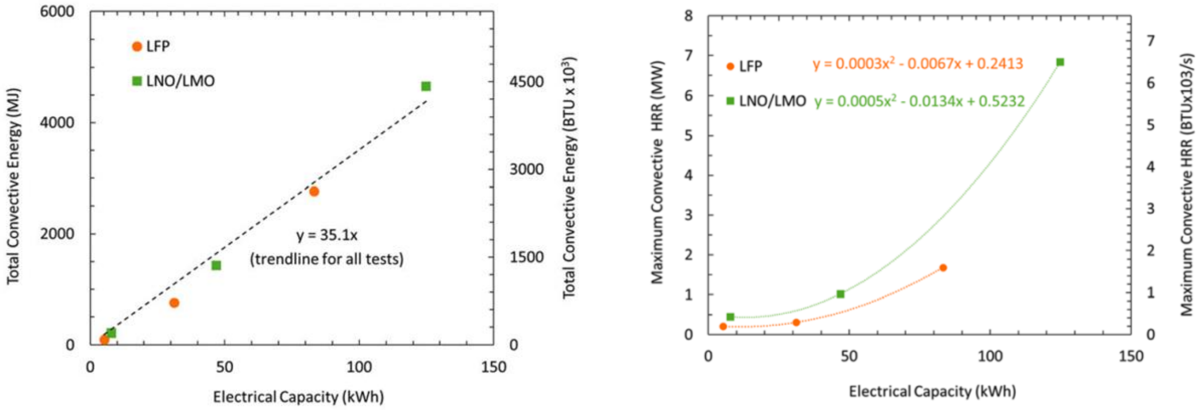



*Figure 5: Total Convective Energy and Maximum Convective HRR correlated to LIB capacities for LFP and LNO/LMO LIB cells* [89]

## 6.3 Ignition Hazards

The hazards of flammable gases vented from a failed LIB cell can pose the potential for a fire or explosion. Without the gases reaching their auto-ignition temperature or exposed to an ignition source no fire or explosion can occur. However, failed LIB cells tend to be their own ignition source, although often delayed from the initial release of vented flammable gases. Two factors that increase the probability of flaming combustion of the vented gases are increased SOC of the LIB when undergoing thermal runaway [49] [96] and an increased number of cells within an LIB installation or higher LIB capacity [77] [54].

## 6.4 Flaming Debris / Shrapnel / Jet Flames

A unique hazard that may accompany a thermal runaway event of an LIB is the violent ejection of flaming debris, shrapnel, and jet flames [43,44]. These hazards increase the area of protection for LIB installations as these hazards can project themselves distances many times the dimensions of the initial LIB. The primary factor that effects the likelihood of this hazard from occurring is if the LIB is at a higher SOC. Failure of an LIB at a higher SOC is known to result in violent eruptions [97]. Zhao et al. [96] identified during failure tests comparing LIBs at 70% SOC and 100% SOC, the LIB at 100% SOC LIB ejected 2.3 times the amount of molten aluminum particles than the 70% SOC LIB during failure.

## 6.5 Explosive Hazards

The vented gases from a failed LIB contain flammable material and in the right conditions can result in an explosion. Additionally, the vented gases are composed of a range of densities that means the flammable gases can accumulate throughout an entire enclosure. The probability of an explosion from a failed LIB cell is low but the severity of an explosion does occur justifies considering this hazard. Three gas properties that define the severity of an explosion are the lower flammability limit (LFL) of the vented gases, flame speed, and maximum adiabatic overpressure [2]. The vented gases from a failed LIB, if allowed to accumulate, can build up past the LFL and if the LIB is in a confined spaced increases the probability of a gas explosion [98]. An experimental study completed by the FAA [77] showed that the LFL, depending on the SOC of the LIB, was 10% and the upper flammability limit (UFL) varied between 35% and 45%. The LFL was determined using the ASTM E681 Standard Test Method for Concentration Limits of Flammability of Chemicals [99]. The other gas properties, flame speed and maximum adiabatic overpressure, are dependent on the concentrations of gas species in the vented gases which in turn depends on the cell chemistry. Baird et al. [2] tested NCA, LCO, and LFP LIB cells and found that the vented gases from the NCA and LCO LIB cells had higher flame speeds and maximum overpressures relative to the LFP LIB cells.

## 6.6 High Voltage

Risks to high voltage is a hazard present in both regular operation of LIB technology and during LIB failure events. Long et al. [100] tested to see if applying water to compromised high voltage LIBs presented shock or electrocution risks to firefighters. The more significant risk of shock or electrocution occurs when the LIB is charging but when the LIB is disconnected the only electrical risk is if one touches both the positive and negative electrodes at the same time. It was determined that even applying a solid water stream directly onto the compromised LIB produced little to no increase in risk of shock or electrocution. However, applying water to the LIB arrangement can affect the non-compromised LIB cells and result in external short-circuits. A significant risk exposure to shock or electrocution when handling LIBs can occur if penetrating or cutting into an LIB cell, regardless of the SOC [101].

## 6.7 Reignition

When an LIB cell enters thermal runaway, internal reactions can help to reignite an LIB even well after flaming combustion has been extinguished. Full-scale fire testing on EVs completed by the Fire Protection Research Foundation [102], experienced this when a flaming combustion from an LIB was extinguished only to reignite 22 hours later. The internal reactions that continue after firefighting operations are exothermic chemical processes that can compound to the point of a second thermal runaway event [45]. To lower the risk of reignition, it is proposed to let the LIB to burn until all active material is decomposed [43,44] [48]

# 7. Fire Incidents of Lithium-ion Batteries

As our world transitions into a modern, electrified, efficient future the application of LIBs has taken hold as an integral technology for future improvement. Proof of this electrification of industry can be seen with Audi discontinuing development of their internal combustion engine and end production by 2026 to focus on exclusively on developing their electric vehicle (EV) fleet [103]. Another major auto manufacturer focusing on EVs is Nissan who also has ended development of its ICE for all major markets except for the US [104]. The applications of LIBs have become ingrained in nearly all consumer products and industrial applications. With this expanded scope of applications, LIB fire and explosion events have brought global attention to this unique hazard.

## 7.1 LIB Cell and Module Level

It is hard to look around one's house or in one's pocket and not find something that is powered by LIBs. These power sources are integral to modern living but not without a certain risk. The fire risk of LIBs came under international spotlight particularly in 2017. Within that year, Samsung had to recall thousands of its new Galaxy 7 phone due to design and manufacturing defects [105]. The reported defects were that the anode was deflected in the upper-right corner of the battery and welding burrs on the cathode compromised the separation between the electrodes resulting in internal short-circuits. These internal short-circuits resulted in the battery entering thermal runaway and lead to many cases of fires and explosions [105]. A month after the recall a US flight was evacuated prior to takeoff due to a Galaxy 7 releasing a "thick grey-green angry smoke" [106]. Also, the FAA reported an increasing number of LIB fire events on planes increasing from 8 incidents in 2013 to 31 incidents in 2016 [107]. These incidents were due to a variety of consumer products (phones, laptops, wireless headphones, e-cigs, etc.) and cannot just be tied to the Samsung defects.

If one small single battery device can result in a fire or explosion, mass storage of LIBs can pose a significant risk. In 2017, a train transporting bulk LIBs through a neighborhood of Houston, USA exploded [108]. The cause of this event was reported to be likely from an external short-circuit that sent an LIB into thermal runaway and propagated to other LIBs to vent a quantity of flammable gases enough to form an explosive atmosphere within the train car. The bulk LIBs that were being transported were meant for disposal and were loose within the car and this transport condition permitted the LIBs to be exposed to external short-circuit abuse leading the explosion. In 2021 a storage facility in Molene, IL, USA caught fire and resulted in 2 weeks of firefighting and over 1,000 homes being evacuated due to toxic gas production from the fire [109]. The fire cause and origin were undetermined but due to a lack of compartmentalization with the storage conditions, thermal propagation between the stored LIBs was possible and permitted such a severe fire and environmental catastrophe.

## 7.2 LIB Pack/Powertrain Level

The next level of LIB installation is the LIB pack, often termed an LIB powertrain when used as the power for an electric vehicle. (EV). The EV, although it have been around for a surprising 150+ years [6], has went through multiple technological developments to get to the LIB powered stage we are currently at with nearly all EVs using an LIB pack as its powertrain. From 2020 to 2021, the global share of new EV registrations was increased by 168% with a 28% increase in the global market of newly registered vehicles [110]. This continued influx of EVs is a step towards decarbonization goals but fire safety is still a challenge that needs to be addressed. A table of selected LIB pack fire and explosion incidents [table 9], has shown a repeated cause of the incident is a short-circuit and crash. Crash preparedness makes sense since it is a personal transport vehicle and an LIB pack used for an EV powertrain would be expected to be exposed to significant shock, vibration, and penetration abuse sources. To compensate for these sources of abuses, an LIB pack is often built around a fortified structure with an IP-rating to protect the LIB modules from the elements.

The other common cause of fire and explosion incidents for LIB packs are short-circuits which is a risk that needs additional attention. At the LIB pack level, it is necessary to have an effective BMS and TMS to ensure that the LIB maintains safe operating conditions. The BMS would be capable of detecting a short-circuit within the LIB while the TMS can maintain thermal balancing caused by the short-circuit. Together, the BMS and TMS can help decrease the probability of a thermal runaway event.

## 7.3 LIB Rack/ESS level

At the largest current scope of an LIB installation is the LIB energy storage systems (LIB ESS). LIB ESS are made of one or a series of LIB racks to provide the demanded quantity of power supply and demand. The capacities of LIB ESSs can range from smaller residential systems of 5-50 kWh up to the world's largest LIB ESS at Moss Landing which can store and discharge up to 1,200 MWh [28]. The LIB ESS is an integral component in better utilization of solar PV power stations and advancing the decarbonization initiative however as addressed in section 5.2.3, an increase in capacity increases the severity of an LIB fire. A table of selected LIB rack fire and explosion incidents [table 10], has shown a repeated cause of electrical failure resulting in thermal runaway of the compromised LIB cell. This cause can be resolved by significant. Improvements to the BMS and TMS. AN LIB ESS is a significant enough risk to justify the cost of an improved BMS to monitor the LIB modules and cells closely and acutely for abnormalities. Redundancies are worth considering since the BMS tends to be the failure point for these larger LIB installations. AN LIB rack tends to be a stand-alone structure similar in proportions to a server tower and an LIB ESS tend to be arranged as a server room. Therefore, an effective TMS that can be used is a hot-cold isle system like server rooms to air-cool the LIB rack and modules and maintain a safe operating temperature.

*Table 9: Selected LIB Pack Fire and Explosion Incidents* [46,68,111,112]

| Date | Location | Incident Description | Possible Cause. |
|---|---|---|---|
| March 2019 | Brabant, Netherlands | A BMW i8 PHEV started to smoke in a showroom | Unkown |
| January 2019 | Florida, USA | A Tesla Model S caught fire after a crash | The crash defromed the LIB initiationg short-circuts, outgassing, and fire |
| August 2017 | Califorina, USA | A Tesla Model X caught fire after crashing into a garage | The crash defromed the LIB initiationg short-circuts, outgassing, and fire |
| August 2016 | Paris, France | A Tesla Model S caugt fire during a promotional tour | Unkown |
| July 2016 | Rome Italy | An EV police car caught fire on the street | Unknown |
| July 2016 | Nanjing, China | The battery pack of an EV bus caught fire after heavy rain | Water immersion caused a short-circuit |
| June 2016 | Beijing, China | An iEV5 caught fire before the landmark of Sanlitum | Might be overheat caused by loose wire connection |
| April 2016 | Shenzen, China | A Wushou Dragon EV bus caught fire | Short-circuit caused by wire deterioration |
| January 2016 | Gjerstad, Norway | A Tesla Model S caught fire while fast--charging at a supercharger station | Short-circuit during charging |
| September 2015 | Hangzhou, China | The battery pack of an HEV Bus caught fire | The LIB pac was out of warranty after 7-year service |
| April 2015 | Shenzen, China | A Wushou Dragon EV bus caught fire during charging in a garage | The BMS failed in preventing overcharing the LIB. |
| October 2013 | Seattle & Tenessee, USA | Two Tesla Model S ran over large metal objects at highway speeds and caught fire | The battery pack was pierced and deformed by the metal objects. Short-circuit occurred and ignited some cells |
| January 2013 | Takamatsu, Japan | The main battery pack caught fire during a Boeing 787 flight from Yamaguchi-Ube to Tokyo | Internal short-circuit |
| January 2013 | Boston, USA | The APU battery pack caught fire and filled the cabin of a Boeing 787 Dreamliner with smoke | Internal short-circuit |
| May 2012 | Shenzen, China | A BYD E6 taxi was collided from rear end by a Nissan GTR at extreme speed. The taxi caught fire after hitting a tree, killing 3 occupants | High-speed collision deformed the high voltage circuit. Arc was triggered from the damaged high foltage circuit, ignitied 25% of the LIB cells and whole car |
| July 2011 | Shanghai, China | EV Bus caught fire | Overheat of LFP batteries |
| June 2011 | USA | A Chervolet Volt used for crash testing caught fire weeks after testing | Coolant leaked over LIB terminals to cause an ecternal short-circuit, resulting in thermal runaway |
| May 2011 | Burlington, USA | A Chevy Volt, which had side-pole impact test 3 weeks ago, caught fire and destroyed adjacent cars | The side-pole impact damaged the coolant system and the battery module. Conductive coolant formed external short-circuit and ignited flammalbe gas vented from cells |
| April 2011 | Hangzhou, China | EV Taxi caught fire | Fire originated within LFP LIB pack |
| September 2010 | Dubai, UAE | Boeing B747-400F carbo plane caught fire | Overheat of LIB |
| January 2010 | Urumqi, China | Two EV buses catch fire | Overheat of LFP batteries |
| July 2009 | Shenzhen, China | Cargo plane caugth fire before flight to the US | Spontaneous combustion of LIB |
| June 2008 | Columbia, USA | The lithium ion battery pack of a modified Prius caught fire during highway running | Loose connection led to battery overheat near loose bolt |
| June 2008 | Japan | Honda HEV caught fire | Overheat of LFP batteries |

*Table 10: Selected LIB Rack Fire Explosion Incidents* [113–116]

| Date | Location | Incident Description | Possible Cause. |
|---|---|---|---|
| April 2021 | Beijing, China | A 25 MWh LIB ESS associated with a 1.4 MW PV array exploded and killed two firefighters | Unknown |
| 2017 - 2018 | Korea | Series of +20 fires at LIB ESS throughout Korea | Innapropriate electrical protection, operational environment, inappropriate installation and integration with BMS, and defects with the manufacturer of the LIB cells |
| November 2017 | Belgium | During commissioning a 20 MWh LIB ESS caught fire and the fixed fire protection was uncessfull in extinguishing the fire | Assumed to be caused by electrical abuse during testing. |
| November 2012 | Arizona, USA | A fire and explosion occurred at a 1.5 MW LIB ESS resulting in severe injuries to 4 firefighters | Internal failure of LIB cell caused by dentrite formation lead to thermal runaway which, without effective fire protection, lead to extensive thermal propogation to rest of LIB |

# PART III – LIB Fire and Hazard Detection, Prevention, Mitigation, and Handling

This third section of the report is intended to present modern fire prevention and mitigation technologies and their applicability to LIB fire hazards. The technologies introduced in the following chapters investigate applications of technologies built inside the battery cells, the sub systems of the battery pack, just outside the battery pack, for full room installations, and technology brought into the hazard by first and second responders. The intended hazard location that is the focus of this report is LIB installations in tunnels and underground facilities. As such, this work has been completed with the assistance of CERN and their CERN fire and rescue service (CFRS). The existing methodology at CERN was provided by CFRS in the form of CFRS procedures [117–122], guidelines [123,124], risk and hazard assessments [125,126], incident reports [127], safety request forms [128–130], and personal tours of the facility [131]. The industries methodology, however, has been derived from a review of practical fire testing (from cell level to installation level), LIB handling recommendations (from manufacturers, international codes and standards, fire research groups, etc.), and tunnel fire dynamics. This is a general summary of these technologies and recommended reading material for depth of study can be found in the referenced texts.

# 8. Lithium-ion Battery Detection Technologies

The scope of this report is to address LIB installations in tunnels and underground facilities, but the idealized detection technology seems impossible since the range of LIB installations vary significantly from single cell LIBs to stationary BESSs. This section will introduce common detection technologies and present their best-practice installations or applications.

When considering the fire hazards and risks of LIB installations, a critical detection threshold is thermal runaway. As such, early intervention to an LIB cell approaching thermal runaway can reduce the probability of a fire or explosion event but that is much easier said than done. Key early detection criteria for LIB configurations are cell temperature (heat), gas monitoring (smoke), and infrared/ultraviolet thermal imaging cameras (electromagnetic). Unfortunately, there is no universal critical thresholds for these detection criteria which can depend on a combination of the LIB chemistry, LIB construction, internal and external thermal propagation inhibitors, battery management system (BMS), size of LIB configuration, state of charge (SOC), and battery treatments (charging vs. discharging). To assist this, the general development of thermal runaway presented in section 4.1 is further expanded by Larsson [61] as a simplified risk assessment of LIBs shown in tables 11.

*Table 11:General Risk Assessment for LIBs including Hazards, Source, Consequence, and Strategies* [61]

| Hazard | Source | Mitgation/Protection Strategy | Consequence (Worst Case) | Possible Mitgation/ Protection Strategy |
|---|---|---|---|---|
| Swelling (but no gas release) | External Heating | If minor, BMS by cooling via TMS | Acute safety typical ok, a balloon of flammable gases have increased fire risks | BMS. Detection and remove / replace cell probability important |
| Gas Release / Venting | External Fire | Fire barriers, fire fighting | Acute Toxicity | Early detection - warning and personnel evacuation. Propogation mitigation (limit problem size/severity). Battery placing. Ventilation. Detox (anti-dote) gas filters. |
| Toxic Gas Emissions | Mechanical crush / deformation / penetration | Battery protected box, reinforced deformation structure, placing of battery | | |
| Corrosive Acid / Gas | | | | |
| Gas Explosion* | External short-circuit | Circuit breakers e.g. fuse | | |
| Electrolyte Leakage | Internal short-circuit | Not possible for cell, propotation protection by system | Increased risk of fire (flammable vapors) and toxicity (of decomposition products) | Ventilation. No heat/ignition sources. |
| High Cell Pressure | | | Spreading out of combustion material, increased fire risk. Ballistic projectile hazards for persons, vehicles, etc. | Cell designed to release gas before extreme internal pressure is reached. Ballistic projectile protection. |
| Cell Case Rupture | Overcharge | BMS, possible cell internal call safety | | |
| Cell Case Explosion | Overdischarge | BMS, possible cell internal call safety mechanisms | | |
| High Temperatures | | | Burn hazards for persons, ignition source | Cooling by TMS (if still operational) |
| Gas Explosion** | | | Damage to building and persons potentially severe (life threatining | Pressure release in battery pack. Propogation mitigation (lower |
| Fire*** | | | Heat release. Fire Source to spread to adjacent structures | Propagation mitigation. Fire fighting. |
| Fire in Battery Cell | | | | |
| Fire in Battery Pack Material | | | | |
| Electrical Voltage Hazards | BMS Fault<br>Mechanical crush / deformation / | Electrical insulation, correct personal handling technique and equipment | From small burn to potential leathal injury | Insulation. Floating ground. BMS. Adequate personnel training on electrical hazards and equipment. |

* Gas explosion of battery vented gases, at relatively low temperature without a thermal runaway, can generate a gas explosion in case of ignition and within the flammability limit

** Gas explosion of battery vented gases, in case of thermal runaway having its own ignition source (e.g. cell temperature higher than the autoignition temperature, spark) in case of within the flammability limit.

*** Fire from the battery cell and/or from fire of non-cell material, e.g. plastics, cables, electronics, within the battery system

Protection strategies highlighted in these tables introduce specific hazards with their corresponding source, consequence, and mitigation strategy. Note that there is no quantified probability, severity, or rating due to the lack of data.

When dealing with LIB hazards there are physical levels of detection that are defined from the proximity to the LIB cell. The closest physical level of detection is referred to as *integrated detection* where the detection technology is integrated within the manufacturing of the lithium-ion cell or battery pack (i.e., monitoring a single LIB cell within a larger LIB installation). The next physical level of detection is *internal detection* where the technology is implemented within the LIB rack (i.e., sensors installed within an LIB rack to monitor a group of LIB modules). The largest scale of physical levels of detection is *external detection* which monitors an entire area that happens to contain LIB installations. It is found that at certain physical levels of detection some detection technology provides great early detection options while others remain average.

Early detection of LIB thermal events is one thing, detection in tunnels is another hurdle. An examination of fire incidents in tunnels and underground stations completed by David Purser [132] has identified several stages between the first detection and evacuation warning that allowed a fire to develop to a serious health and safety hazard. The noted stages identified by Purser are the pre-alarm, decision by security staff, investigate fire site, appraisal of site, report back up management chain, and wait for direction. These identified stages do not summarize all fire incidents that occur in underground facilities since existing protocol may have activated the general alarm at an early stage. However, it does fit the pattern of most major fire in underground facilities and warrants appropriate detection protocol. Common detection systems used in tunnels include line type heat detection, smoke detection, flame detection, visual image fire detection, CCTV system, spot heat detection, and/or CO2/CO sensing fire detection [133]. These detection technologies and others are addressed in the following sections.

## 8.1 Integrated Battery Devices

Regardless of the source of abuse, the early detection of a thermal runaway event is crucial. The physical level of integrated detection is at the forefront of early detection for LIBs. Work done by Diaz [88] identified five early detection criteria:

1. Terminal voltage using the BMS
2. Unusual gases emitted
3. Internal battery temperature
4. Current variations as indication of short circuit
5. Mechanical deformation using a strain gauge sensor.

Catching an LIB cell experiencing one or multiple of these early detection criteria may not prevent the cell from reaching thermal runaway but immediate response may prevent neighboring cells from experiencing thermal runaway. Of these five detection criteria, numbers 1, 3, and 4 are the common detection methods used at the integrated level of detection. The integrated detection technology used to monitor these critical criteria can be

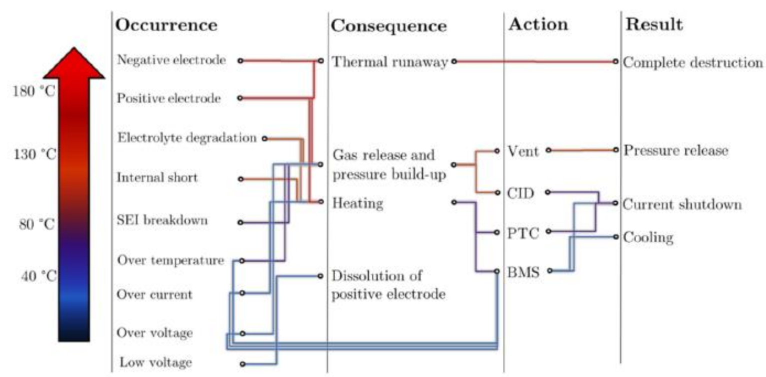



*Figure 6: Event tree connecting occurrences within an LIB to the activation of safety devices, and ultimate outcome* [134]

best visualized in an event tree [fig. 6] made by Finegan [134] which connects the thermal evolution of an LIB cell with the activation of safety devices and the result of the action. The integrated detection devices used to monitor these criteria are detailed in the following sections. When implemented together, these devices can significantly improve LIB operation safety [45].

### 8.1.1 Current Interrupter Device

The current interrupter device (CID) is generally synonymous to the safety relief vent. The CID is a metallic plate that is a part of the positive terminal of the LIB cell. The working principle of the CID is when pressure builds up inside the LIB cell the metallic plate displaces to the point of breaking positive terminal from the circuit and preventing current flow [45].

This device does not discriminate the response based on the type of abuse the LIB cell is exposed to (physical, thermal, electrical) but instead monitors over-pressurization caused by any of the sources of abuse. Unfortunately, not all LIB cells have a CID. For instance, pouch style cells do not have a safety relief vent and as such no CID [45].

### 8.1.2 Positive Temperature Coefficient Material

To protect an LIB cell from unwanted high current, a positive temperature coefficient (PTC) material is integrated into the manufacture of LIB cells [136]. The PTC material is generally made from a conductive polymer that at a safe temperature range completes the circuit of the LIB. Outside of this safe temperature range, the PTC material will melt and break the circuit [45]. In addition to early detection to high current exposure this device also can be triggered by excessive ambient temperatures found during fire events.

### 8.1.3 Battery Management System

Often called the "brain" of the battery system [61], the battery management system (BMS) has a series of sensors to monitor and control critical operations of the battery. For smaller LIB systems up to the LIB module level the BMS is sometimes called a protection circuit module (PCM) which may have limited monitoring capabilities [61]. The BMS or PCM can be electronic or mechanical and nature while servicing an LIB cell, module, rack, or ESS [45]. At the larger levels of LIB installations (LIB pack and ESS), the BMS is a hierarchy of BMSs with a secondary BMSs monitoring each LIB module and a primary BMS monitoring the secondary BMSs [61]. The criteria of the LIB that the BMS monitors have been identified from testing [49,61,88,137,138] and are:

1. Temperature of the batteries/cells and coolant (° C).
2. Cell voltage and total voltage (V).
3. Charge level of the batteries (SOC%).
4. Current draw (A).
5. Depth of discharge (DoD)
6. Coolant flow (l/min).
7. Available power: Calculated based on voltage, current draw and battery temperature.
8. Ensure that all cells in a battery module are charged equally.
9. Calculate the health status of the batteries and calculate the available charging capacity in relation to when the batteries were new (SOH%).

When any abnormal signal is detected, the BMS can triggers a warning or send an alarm signal [138]. The 9 criteria that the BMS can monitor allows the BMS to detect a thermal runaway event and even responding with a mitigation response. Monitoring all criteria allows the BMS to prevent and mitigate:

- Overvoltage: too high charging voltage
- Overcurrent: too high charging current
- Undervoltage
- Overcharging: charging continues after full charge
- Deep discharge
- Too high or low temperatures
- Earth faults, for some cases

If a dangerous condition is detected by the BMS monitors, the battery pack can shut down its current treatment status (discharging or charging), begin thermal management by transmitting an alarm signal and/or operate the internal cooling system, and locate the faulty LIB cell or module. The importance of this detection technology increases proportionally with the LIB capacity of the installation. A single cell LIB would not warrant a state-of-the-art BMS however an LIB installation at the pack level or higher poses a significant level of risk that would warrant consideration. Work done by Larsson [61] found two points of improvement for BMS, better sensors and better and faster algorithms. Using more sensors with higher accuracy is the first step to improving detection capabilities of the BMS and limiting the time from event occurring, detection, and protective action. The note on faster algorithms refers to data process capacity and finding anomalous cells before failure. Larsson even proposes having individual cell circuit breakers to bypass the anomalous cells but acknowledges it being currently commercially non-viable. Regardless of the number of criteria monitored by the BMS it is important to have the capabilities to validate BMS failures as well as sensor failures by having increased redundancy.

## 8.2 Smoke Detection Technologies

Smoke detectors are available in a variety detection options such as air sampling, linear beam, video, ionization, photoelectric, and combination ionization/photoelectric smoke detectors. Each smoke detector type monitors for smoke or particulates generated from a fire but certain air sampling detectors can also sample for specific gases for a more accurate detection option. These detection technologies can be proven effective in many installation locations since their activation occurs where fire gases accumulate, and LIB fire gases can build up everywhere since it is a mix of lighter and denser gases [49]. Tests of detection technologies of LIB fires completed by Wang et al. [45] have shown smoke and combination smoke-heat detectors can effectively detect a thermal runaway event for LIB fires.

### 8.2.1 Active Air Sampling

An active air sampling detection system operates by monitoring both the current ambient conditions unaffected by applied hazards and the hazard area. By monitoring both inside and outside the hazard area a base level can be determined. A user defined tolerance is set for allowable gas or particulate species gradient between the two monitoring environments and if it is found to be more than the defined threshold the fire alarm control panel can be set to go to alarm. By using a floating ambient condition this helps prevent a false alarm, for example using a propane powered forklift in a warehouse monitored with this system can account for the exhaust of the forklift and raise the threshold for sending and alarm signal. These types of detection networks can be set to a highly sensitive tolerance which has been proven effective in early detection of LIB fire events.

Active air sampling systems have earned trust within the marine industry, specifically aboard military vessels and within engine compartments of general marine vessels, due to this method's high sensitivity. When implementing active air sampling systems in marine compartments the monitored enclosures are well compartmentalized and tightly sealed which make this detection system very effective and efficient [94,139]. However, within a tunnel or underground facility with significant volume and air changes to monitor an entire section requires an increased cost as the number of air sampling units increase to compensate. These systems are conversely highly effective as localized detection networks instead for example when installed into a server tower or battery rack. In this example the towers and racks are usually cooled using mechanical ventilation (hot and cold isles) and the air sampling takes advantage of the ventilation system to decrease the travel time of particulates and volatiles to the main unit. An experimental study [140] on fire detection in buses show that active air sampling detectors are less sensitive to high airflow at the position of the detector/sampling hole. This indicates that this detection technology would be most effective if implemented at the internal level within an LIB pack powertrain or a stationary LIB rack installation to provide early detection of an off-gas event or thermal runaway.

### 8.2.2 Linear Beam

A linear beam smoke detectors use the working principle of projecting an infrared (IR) light to a receiver. This can be accomplished as an end-to-end arrangement with separate light transmitter and receiver or as a reflective arrangement where the transmitter and receiver is a single unit with a retroreflector bouncing the transmitted light back to the receiver. If the receiver does not measure a certain percentage of the transmitted light an alarm signal will be sent. This type of smoke detector is useful for monitoring large open area's and is usually found in atriums, theaters, and airport terminals. As such, this detection technology may be effective in monitoring linear sections of tunnels. However, as with all smoke detectors at the external level when there is enough smoke built up to cause an alarm signal to be sent, multiple LIB cells have likely reached thermal runaway or surrounding material has been ignited by the first thermal runaway event. This delay of detection can be deadly when dealing with tunnel hazards [132].

### 8.2.3 Ionization and Photoelectric

Two other smoke detection technologies, ionization and photoelectric are commonly found in household smoke detectors. Ionization smoke detectors function by use of a substance called Americium-241. An electronic circuit is created with a flat metal plate electrode connected to each side of the battery and the circuit is connected by ionized air created by the Americium-241. If a fire occurs and smoke enters the detector and gets between the two polarized plates, the ionized air will bond to the smoke and reduce the circuits current. The circuit is monitored, and an alarm signal is sent when the circuits current is reduced. The working principle of a photoelectric smoke detector is however more like the linear beam detectors. The key difference between the two is that the light transmitter and the light receiver are perpendicular to each other within the smoke detector instead. This means that when light is received by the sensor an alarm output will be sent. In a fire event with smoke present, the smoke can enter the detector and cause the transmitted light to scatter and send light to the receiver causing the alarm output. Additionally, these two technologies can be combined into a single smoke detector called an ionization/photoelectric smoke detector. The ionization smoke detectors are effective for fast burning fires while the photoelectric smoke detectors are better for small smoldering fires. These simpler technologies are also found in combination with other types such as heat detectors and gas monitors. LIB fire testing to compare smoke detection technology [45] has shown combination smoke-heat detectors have the quickest detection time compared to smoke and heat detectors. This study did not however include active air sampling which based on performance testing would likely outperform even combination smoke-heat detectors. The benefit of this detection technology is the lower cost point and smaller size. Due to these benefits, installation of either ionization or photoelectric detectors at the internal level to provide early detection of an off-gas event preempting a thermal runaway or early stages of first LIB cell undergoing thermal runway.

## 8.3 Optical Flame Detectors

Found in some of the most hostile and hazardous environments, optical flame detectors are visual-based detectors that monitor a field of view for flames. This detection technology monitors a specific wavelength and frequency of the electromagnetic spectrum to visually detect a thermal event within milliseconds of occurring. Often installed in turbine and engine rooms or chemical processing plants for early detection, optical flame detectors have been proven effective when implemented in tunnels as spot fire detectors. The detectors are visual-based and operate on a line of sight, so physical obstructions will need to be considered to prevent detection delay.

Optical flame detectors come in a variety of styles based on which band of the electromagnetic spectrum is being monitored: infrared (IR), ultraviolet (UV), and combination UV/IR detectors. This detection technology is effective for fires that rapidly occur and monitoring large areas but regarding LIB fire development, optical flame detectors may provide a delayed time for detection. When flaming combustion occurs from an LIB hazard at least one LIB cell has reached thermal runaway and the neighboring cells are close behind. This is delay may be considerable but additional testing would be required to quantify the potential delay. Additionally, the critical temperature to monitor is the cell temperature which must be done with discretion from the exterior of the LIB pack using an optical detector [49]. When the true LIB cell temperature cannot be accurately measured from the exterior, recording the temperature changes over time would be the next best indicator of an overheating LIB cell, module, pack, or rack.

### 8.3.1 Infrared Flame Detector

The infrared (IR) detectors use a pyroelectric sensor to detect a change in IR radiation intensity, but this detector type can be further subdivided into single frequency and multi spectrum IR detectors. Single frequency IR flame detectors operate in a narrow single band usually around 4.4 micron. This band means the detector is blind from the sun's radiation (0.38 – 0.76 microns) and other smaller wavelengths (welding, lightning, and X-rays, sparks, arcs, and corona) but instead monitors the prominent emission band for hydrocarbon fueled fires. Multi spectrum IR detectors however use multiple sensors, usually three sensors, at different IR bands which require a simultaneous detection at the different IR band to pass on an alarm output signal. This synchronous detection method means false alarms are less likely but will detect slower than a single frequency IR detector. The physical limitations of both IR detectors are weather conditions that can block the detector lens with vapors, water, or ice as this will obstruct the pyroelectric sensor and prevent active monitoring. The hazard types ill fitted for IR detectors would be burning metal, ammonia, hydrogen, and sulfur fires which do not produce significant IR radiation within the monitored bands. The general composition of fire gases from an LIB tested within an inert environment [78] was roughly 50% volatile organic compounds (VOCs), 45% carbon dioxide ($CO_2$), and 5% HF. Note that the provided species concentrations are produced in the absence of flame and as such allows measurement of unstable species that would not have existed in non-laboratory setting. However, the large concentration of VOCs indicates a hydrocarbon-based fire that would be ill fitted for IF detectors. Due to the working principles of this detection technology, the only applicable installation level is at the exterior level and would monitor the area of LIB use.

### 8.3.2 Ultraviolet Flame Detector

Ultraviolet (UV) detectors use a sensor tube called a deuterium discharge (D2) lamp to monitor radiation emitted at a range of 0.18 – 0.25 microns. This sensor range is chosen to prevent false alarms caused by solar radiation while monitoring a range of radiation present in most all fires. Although solar radiation is considered, other potential light sources like lightning, sparks, arcs, and coronas can potentially cause a false alarm. The types of fires UV detectors are subtle for are hydrocarbon, metals, sulfur, hydrogen, hydrazine, and ammonia. With the large concentration of VOCs measured in LIB fire gases, a UV optical flame detector would provide the best detection for this type of detection technology. The delay of detection until flaming combustion is still a significant concern for this detection technology.

### 8.3.3 Combined Flame Detector

Both detection technologies can be combined, UV detector and a single frequency IR detectors pyroelectric sensor, to create a combination UV/IR detector. This type of detector is highly effective for hydrocarbon fires but is just as ineffective as an IR detector for certain hazards since sending an alarm output requires detection from both radiation bands. Thus, it would be likely that this combination would cause additional delays of detection caused by the ill-suited IR detector portion of this detector.

## 8.4 Heat Detectors

This detector technology is often integrated into smoke detectors, but they of course provide a different detection method. Heat detectors are designed in two options with very different detection technologies: fixed temperature and rate-of-rise heat detectors. A fixed temperature heat detectors working principle that at a specific temperature an alarm signal will be sent. This can exist as a spot heat detector, which looks like a common household smoke detector, and a continuous line heat detector. A spot heat detector functions using either a bi-metallic plate or a heat sensitive metallic alloy that at a manufacturer listed temperature an electric circuit will change state and send an alarm output. A continuous linear heat detector consists of a cable with two wires protected by a weak thermal insulator. During a fire scenario the insulation will melt at a specific temperature and when the two wires come into contact an alarm signal will send. The rate-of-rise heat detector works differently than the previous mentioned heat detection technologies. Instead, the temperature is monitored using typically an electric thermocouple that will send and alarm signal if the measured temperature rises a defined value within a minute, this is typically set at around 15 °F (8.3 °C)/min. This heat detection technology can be combined with the fixed temperature concept but will still only send an alarm output when the rate-of-rise threshold is reached. This type of detection technology can be implemented at the internal and external level but testing [45] suggests that heat detectors provide delayed detection capabilities compare to smoke detectors and would thus not be suitable for the early detection of an LIB fire.

## 8.5 CCTV Camera Network

A network of closed-circuit TV (CCTV) cameras is typically installed for the sake of personnel and site security. This multilevel of security can provide great opportunities in the realm of fire detection. When site personnel cannot verify a potential fire event due to increased personal risk, a well-placed CCTV camera can provide an immediate status confirmation. This technology's effectiveness depends on no visual obstructions and regular maintenance/cleaning. Additionally, the resolution of camera and user heads up display (HUD) decides if the operator can see what is happening.

To improve the effectiveness of this technology, artificial intelligence (AI) or a visual algorithm [141,142] can be integrated to automatically detect smoke and/or flames. The sensitivity for this altered detection model can be adjusted to accommodate for transient conditions such as steam plumes generated by vehicle exhaust during cold days or general personnel movement. This altered detection method has been tested inside engine rooms and chemical processing plants. Thus, CCTV cameras can be trained to monitor for excessive smoke production or fire within a tunnel or industrial hazard. As with optical flame detectors, this type of detection technology would provide delayed detection, likely past the point of thermal runaway for the first LIB cell.

## 8.6 Gas Monitors

Often used in chemical processing plants and hazardous material (HAZMAT) operations, gas monitoring can be used to define the current species concentrations of oxygen, various combustible, flammable, and toxic species. Common species found in LIB fire gases that can be monitored are carbon monoxide (CO), carbon dioxide (CO2), oxygen, (O2), hydrogen (H2), hydrocarbons ($C_MH_MO_Z$), hydrogen fluoride (HF), and hydrogen sulfide ($H_2S$). Gas monitors can exist in both a portable format for HAZMAT operations and fixed installations. When monitoring fire and toxic hazards, a fixed monitoring system can have an advanced level of safety when the system is designed to have a heads-up-display (HUD) showing the current species concentration within the hazard area. Monitoring these species concentrations may prove to be a great early detection technology because gas release (off-gassing) can occur before or without an LIB reaching thermal runaway [61]. To make this detection technology truly effective and closely monitor LIB installations, the detector would need to be installed at the internal level within an LIB pack powertrain or a stationary LIB rack where the gases would build up. At the external level, gas monitors show to be effective for monitoring larger LIB installation confined in an enclosure where gas buildup is possible. It is not known if gas monitors within tunnel installations would be effective in monitoring LIB hazards and future testing is recommended.

The gas monitoring technologies vary depending on the specific gas to be monitored but the common types are catalytic, infrared, electrochemical, and metal oxide semiconductor sensors. The catalytic and infrared sensors are designed for the combustible and flammable species (CO, CO2, H2, CNHMOZ) while the electrochemical and metal oxide sensors are best for the toxic species (HF, H2S) [49]. This technology can be highly sensitive and be very effective early detection devices if a specific gas species is chosen to be monitored. a stage preempting the critical thermal runaway event is the release of LIB cell material in a stage called off-gassing. This all suggests the probable effectiveness of gas monitors as an early detection technology if all LIB installation variables are considered and a specific species and concentration can be determined for the final installation. LIB abuse testing [78] has shown that monitoring hydrocarbons at the interior level, within the LIB pack or rack, may be the most effective detection option since the critical failure mode (off-gassing) would be detected regardless of the rate of temperature increase occurring inside the LIB. The gas generation of an LIB cell experiencing thermal runaway produces both flammable and toxic species but the trouble for detection is the species concentration varies depending on the LIB chemistry, SOC, capacity, and ambient conditions. Due to the wide range of possible gas species generation, multiple gas monitors may be a recommended detection, e.g. a detector for toxic gases (CO2 and HF) and a detector for flammable gases (VOCs, $H_2$, and hydrocarbons) [61].

# 9. Lithium-ion Battery Fire Response Methods

An abused LIB cell approaching or experiencing a thermal runaway event can have the severity, and in some cases the probability, of a fire/explosion incident reduced by immediate fire response. The response would be one or a combination of fire mitigation, suppression, and extinguishing methods. To prevent misinterpretation, the fire response methods *fire prevention, mitigation*, *fire suppression*, and *fire extinguishment* will need to be defined. A fire prevention method would be safety devices or modifications installed within the LIB cells to prevent thermal runaway in an abused cell. A *fire mitigation* method would be technology or devices integrated within the LIB cell to improve the thermal stability or within the LIB module/pack/rack to prevent cell-to-cell thermal propagation. Fire mitigation exist as improved cell chemistry, packing material, and integrated safety devices. *Fire suppression* methods are systems designed to limit the growth and spread of fire and are generally active fire protective systems [143]. These systems are intended more for allowing safe egress of occupants. A *fire extinguishing* method is a system designed to stop a fire completely by removing one of the sides of the fire tetrahedron: heat, oxidizer, fuel, and self-sustaining chain reaction. The fire extinguishing method is difficult since during a thermal runaway event an LIB cell can self-generate heat (electrochemical reaction) and oxygen (cathode decomposition) making the hazard prone to catching fire [144]. When implementing a fire response method, the stage that the LIB cell is at regarding thermal runaway is important. The stages of fire development an abused LIB experiences are before the first LIB cell reaches thermal runaway, first LIB cell undergoes thermal runaway, growth stage of LIB fire, peak stage of LIB fire, decay stage, and possible secondary growth stage (re-ignition hazard). Throughout these stages for LIB fires, the best method for fire control is to directly cool the LIB cells and protect neighboring fuels. A notable concern with cooling a fully involved LIB cell is that when flaming combustion is stopped the failed cells will continue to vent toxic and flammable gases requiring a different hazard response. A review of fire gas handling options is found in chapter 9. This chapter is intended to address possible fire response methods for LIB hazards applied at the integrated, internal, and external level.

## 9.1 Integrated Level Fire Protection Methods

A safer LIB is accomplished by first avoiding and second managing heat and gas generation. Unless the LIB thermal runaway event was caused by thermal abuse from an external fire, the source of heat and gas generation originates from the failed LIB cell(s). Therefore, mitigation of heat and gas generation can be accomplished at the LIB cell level by modification of one or a combination of LIB chemistry, structure, design and/or internal safety devices [45,145] [145]. All major components of the LIB cell (electrolyte, cathode, anode, separator, safety devices) are points of research and development. [111]

### 9.1.1 Electrolyte Fire Safety

The use of a nonaqueous combustible electrolyte makes LIB technology inherently hazardous. The common electrolyte used by LIB manufacturers is a solution of nonaqueous solvent (usually a mixture of cyclic and acyclic carbonate solvents), inorganic lithium salt (usually $LiFP_6$), and some additives [144]. The cyclic solvents used within an LIBs electrolyte have a higher flashpoint than non-cyclic solvents but still have rather low flashpoints. (i.e., diethyl carbonate (DEC), dimethyl carbonate (DMC), and methyl ethyl carbonate (EMC) have flashpoints of 33 °C, 15 °C, and 22 °C, respectively [146]. This low thermal stability of the solvent makes the nonaqueous electrolyte the first component to react to LIB cell abuse and is identified as the main fuel for the flaming combustion [147]. Testing by Wang et al. [148] has shown that if the carbonate content within the electrolyte is reduced and exposed to temperature above 100 °C the out-gassing can be minimized. Mitigation of the flammability issues of LIB electrolytes has been pursued in two directions: use an inherently non-flammable electrolytes or use flame retardant additives [19].

Non-flammable electrolyte come as solid-state or solid polymer electrolytes. These feasible solutions provide non-volatility, low flammability, easy processability, and electrochemical and chemical stability to the LIB cell but can come with a high cost and limiting performance quality [45]. The cost prohibitive aspect of the current technology may be flipped soon though since solid electrolytes can remove the need for high integrity sealing of the cells thus reducing cost [149]. Testing and research continue for non-flammable electrolytes but until large-scale commercial viability other fire mitigation like flame retardant additives may be the best viable option.

*Table 12: List of common flame retardant additives for LIB electrolytes* [144]

| Abbreviation | Full Name |
|---|---|
| $BMP\text{-}PF_6$ | 1-Butyl-1-methypyrrolidinium hexafluorophosphate |
| CDP | Cresyl diphenyl phosphate |
| DMMP | Dimethyl methyl phosphate |
| DPOF | Dipenyloctyl phosphate |
| HMPN | Hexamethylcyclophosphazne |
| IPPP | 4-Isopropyl phenyl diphenyl phosphate |
| $[NP(OCH_3)_2]_3$ | Hexamethoxycyclotriphosphazne |
| TEP | Triethyl phosphate |
| TMP | Trimethyl phosphate |
| TMP(a) | Trimethyl phosphate |
| TMP(i) | Trimethyl phosphate |
| TPP | Trimethyl phosphate |
| TTFMT | 2,4,6-Tris(trifluoromethyl)-1,3,5-triazine |
| TTFP | Tris(2,2,2-trifluoroethyl) phosphite |

The four main categories of flame retardant additives for LIB electrolytes are phosphates, phosphazenes, phosphides, and ethers [19]. Kong [144] tabulated the types of flame retardant additives used for LIB electrolytes shown in table 12. Testing of several electrolyte additives [147,150–153] has shown increased thermal stability and/or overcharge protection. The working principle of flame retardant additives is that when the additive decomposes in a thermal event, phosphorous or fluorine radicals are generated which react with hydrogen radicals that disrupt the LIB fire’s chain-reaction mechanism [154]. These fire-retardant additives do not come without their own baggage, the quantity of additives need to achieve non-flammability status would significantly reduce LIB cell performance and some additives increase the rate of degradation for LIB components (cathode, anode, and separator). It is not known yet the long-term effect these flame retardant additives have on the cell lifetime [19].

### 9.1.2 Electrode Fire Safety

The electrodes within an LIB cell are more thermally stable than the electrolyte but still contributes to the failure and resulting thermal runaway event. The cathode electrode can be modified by using different coatings [155–158], substituting certain metals [159,160], and doping [158,161] to provide increased thermal stability. The anode electrode can be modified by using surface modifications [162] and certain electrolyte additives [163,164] to provide increased thermal stability. Tests of different anode materials [165–167] has shown using LTO for the anode provides a safer LIB cell compared to graphite.

### 9.1.3 Separator Fire Safety

The two operational functions a separator provides is preventing direct contact between the electrodes and provide a path for the exchange of lithium-ions during battery treatment. The separator is a semi-porous material to allow the exchange of li-ions but if allowed to heat to a melting point the separator's pores can close and stop the transfer of li-ions. AN LIB's separator is built of is a semi-crystalline polyolefin material, polyethylene (PE) and polypropylene (PP), which can be combined in the form of a PE-PP bilayer [168] or PP-PE-PP trilayer [169,170]. The melting point of PE is recorded at varying temperatures of 130 °C [171], 135 °C [172,173], and 140 °C [174] whereas the melting point of PP is recorded at a higher temperature of 160 °C [174] and 165 °C [171–173]. Thus, the intention for both a PE-PP bilayer and PP-PE-PP trilayer is that when the temperature of an LIB cell increases, towards the cell entering thermal runaway, the PE layer melts closing the ionic conduction pathways between electrodes in a process known as a separator shutdown [173]. The separator shutdown process takes time, and this means that during separator shutdown the internal reactions within the LIB cell will continue and as a result the battery will not start to cool down during and possibly not even after separator shutdown [174]. The additional layer consisting of PP, with its higher melting point, inside the separator is intended to retain the integrity of the separator and continue to prevent direct contact between electrodes [175]. The 20 – 35 °C melting point buffer between the PE and PP layers of the separator is designed to protect the overheating LIB cell from reaching thermal runaway but if the separator shrinks or melts, thermal runaway is inevitable [171]. Newer separator technology developed to improve separator shutdown are ceramic-coated separators [176–182] which improve the separators integrity at higher temperatures to delay failure of the separator. One successful application of ceramic-coated separators was created by Separion™, whose product made of polymeric non-woven poly(ethyleneterephtalate) (PET) and ceramic nanoparticles has proven to remain stable at up to 210 °C [183]. In a lain penetration test of an 8 Ah LIB pouch cell, the separator did not reach temperatures exceeding 58 °C as opposed to 500 °C for the same cell using PE separators [171]. However, performance testing of shutdown separators in large LIB installations have shown reduced safety benefits caused by higher battery voltage which leads to separator breakdown [172].

## 9.2 Internal Level Fire Protection Methods

The integrated level of fire protection has been summarized through modifications not within the LIB cell but exterior to the cell to limit thermal propagation between cells.

### 9.2.1 Battery Management System and Thermal Management Systems

In integral safety device for monitoring and maintaining operational conditions for an LIB is the BMS. However, as recognized by historical LIB incidents [section 6] the BMS is not always sufficient to guarantee safe operation. The BMS monitoring capabilities has been defined within section 7.1.3 but what about the response capabilities. Working in unison with the BMS is the thermal management system (TMS) that is available at the LIB pack and rack level. The purpose of the TMS is to maintain optimum operating temperatures of 20 - 40 °C [184,185] and as such required heating and cooling capabilities. When the BMS registers an LIB cell or module below the optimal operating temperature external heating devices, generally installed on each LIB module, activate to raise back to optimal [186]. This is more common for LIB packs as EVs operate outdoors and can have a wider range of ambient temperatures [78]. When the BMS registers temperatures above optimal, cooling methods are applied to lower the temperature back to optimal. The cooling methods used by the TMS include one or a combination of spacing [187–189], air cooling (forced airflow) [190–192], liquid cooling [193,194], phase change material (PCM) cooling [184,195,196], or heat pipe cooling systems [197–199]. The more sophisticated the BMS and TMS is, generally the more expensive the system becomes [171]. However, both the BMS and TMS are mission critical to maintaining a safely operating LIB and without a redundant protection system the LIB is likely to experience a thermal runaway event.

### 9.2.2 Passive Mitigation Strategies

The mitigation strategies offered by the BMS and TMS combination are active methods to mitigate thermal runaway propagation within an LIB through dissipation of heat and for the air-cooling system fire gases too. Passive methods to mitigate thermal runaway propagation within an LIB consist of spacing between LIB cells, physical barriers, and different cell arrangements. Work done by Lee et al. [3] has fire tested dense arrays of fully charged LIB cells with different passive mitigation strategies within a wind tunnel to track thermal runaway propagation within well-defined conditions. The different mitigation strategies used were no gap (constant), 5 mm air gaps, perforated stainless steel barrier, intumescent barrier, and ceramic fiber board barrier. Although none of the tested mitigation strategies totally prevented propagation, the physical barriers significantly decreased propagation rates. Ceramic fiber boards provided the greatest effect of delaying thermal runaway propagation by a factor of 30 but the non-permeable design would likely interfere with the BMS and TMS combination. The second-best passive mitigation option was found to be the perforated stainless-steel barrier. This option would likely not interfere with the BMS and TMS but does come with a significant weight concern when compared to the other options. In addition to monitoring thermal runaway propagation within the LIB cell array discoveries were made regarding impacts to fire gas generation and cell-to-cell heat transfer contributions. The chemical heat generation was constant between the tests but the tests that had both gaps and barriers noted an increase in production of TCH, CO, $CO_2$, and $H_2$. The heat transfer contributions determined from the fire testing showed that heating of downstream cells breaks down as 50% from flaming combustion of ejected LIB cell material, 20% from direct cell-to-cell conduction, and 30% from convective and radiative transfer between cells and conduction through surrounding boundary layer [3]. A further improvement for passive mitigation strategies for LIB installations is to implement complete compartmentalization of LIB modules (i.e. if 10MW of LIB ESS is needed, limit the max capacity of single LIB installations to 1 MW and have 10 sperate LIB racks partitioned with fire and explosion rated dividers) [200].

### 9.2.3 Operating within Inert Environments

An interesting mitigation option that is not truly active or passive mitigation options is operating an LIB within an oxygen reduced environment. An experimental study completed by Weng et al. [201] explored the effects of dropping ambient oxygen concentration to 12% from 21%. An array of LIB cells was subjected to abuse leading to thermal runaway of one cell which was allowed to propagate to the other cells within the array. The tests showed operating an LIB 12% oxygen ambient concentration reduced the thermal-runaway propagation rate by 44% and additionally decreased the mass loss rate and flaming combustion. However, the decreased concentration of ambient oxygen did not have an influence on the max cell temperature.

## 9.3 Fire Suppression and Extinguishing Systems

Due to the stored electrochemical energy within LIB cells and its propensity for self-generation of heat and gases caused by internal reactions between cell components, heat dissipation of the failed cells is mission critical during a fire incident. As previously defined, a suppression system can limit the growth and spread of fire while an extinguishing system is designed to cause complete cessation of flaming combustion [143]. A combination of suppressing and extinguishing is what is needed to best address LIB fire hazards. What needs to happen to protect an LIB hazard is to first cool failed LIB cell(s) and neighboring cell(s) (suppression) and if flames are present the flames need to be extinguished (extinguishing). This is to prevent propagation of thermal runaway and thus decrease the severity of the fire incident. This is particularly true for larger systems like at the LIB pack or rack level, as it has been shown to be more important to cool the LIB to prevent thermal runaway propagation than to extinguish flaming combustion [111]. The basic method of suppression for an LIB fire is the cooling method while chemical flame inhibitors are what is needed for extinguishing

[45]. In addition to cooling and chemical inhibitors, other fire protection options for LIBs are smothering and isolation. A unique challenge with LIB fire hazards is the stranded energy after a fire has been extinguished, there have been occurrences of reignition hours and even days after the fire has been extinguished [202]. Extended protection should thus be considered to protect LIB hazards due to the internal exothermic chemical reactions. This fire protection method is like methods used for protecting smoldering fire hazards for hours after the fire incident.

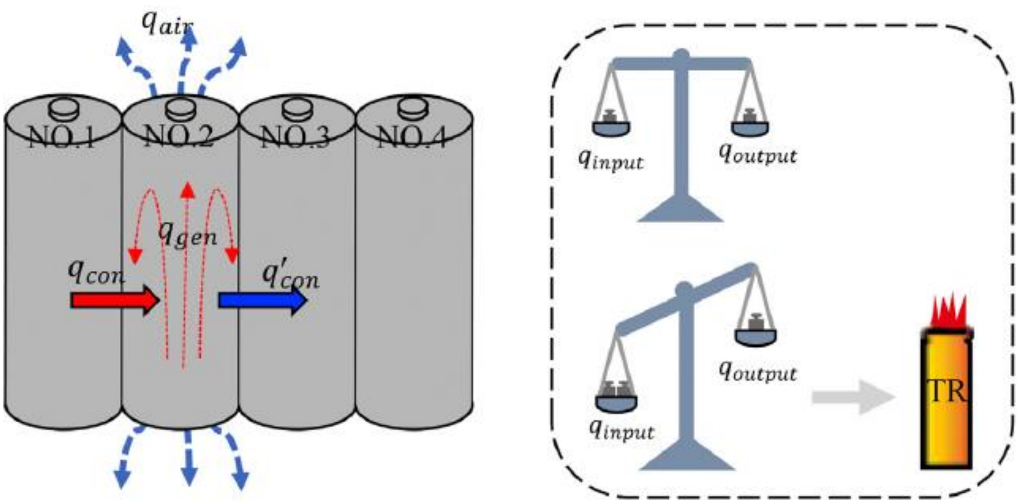



*Figure 7: Heat Transfer Balance Schematic for cell-to-cell Thermal Propogation* [96]

To understand where fire protection systems need to be implemented the process of thermal runaway propagation between cells needs to be better defined. Thermal runaway is simply when the heat input rate to an LIB cell is greater than the heat output rate. As important the first failed LIB cell has in fire development, activation of a fire suppression or extinguishing system occurs after the first cell fails and is intended to address the safety of the remaining LIB cells. For the subsequent LIB cell(s) affected by the failed cell(s) the heat input rate is the sum of the heat conduction rate ($q_{con}$) and the reaction exotherm rate ($q_{gen}$) while the heat output rate is the sum of the natural convection heat dissipation rate ($q_{air}$) and the heat conduction output rate ($q_{con}$'). Work done by Zhao et al. [96] has proposed this heat balance formula and further defined the components of the heat transfer.

$$q_{con} = A\,\lambda\,\frac{T_1 - T_2}{\delta} \quad (7)$$

$$q_{gen} = \Delta H\, M^n\, A \exp\left(-{}^{E_a}/_{R\,T_2}\right) \quad (8)$$

$$q_{air} = h\,(T_2 - T_E)\,A_2 \quad (9)$$

$$q'_{con} = A\,\lambda\,\frac{T_2 - T_3}{\delta} \quad (10)$$

$$q_2 = q_{gen} + q_{con} - q'_{con} - q_{air} = \Delta H M^n A exp\left(-\frac{E_a}{RT_2}\right) + A\lambda\frac{T_1 - T_3}{\delta} - h(T_2 - T_E)A_2 \quad (11)$$

Where $A$ is the heat conduction area, $\lambda$ is the thermal conductivity, $T_1$is the average temperature of cell No. 1, $T_2$is the average temperature of cell No. 2, $T_3$is the average temperature of cell No. 3, $T_E$is the average temperature of the environment, $\delta$ is the thickness of heat-conducting object, $\Delta H$ is the reaction calorific value per mass, $M^n$ is the mass of cell, $h$ is the convection heat transfer coefficient, $A_2$is the natural heat dissipation area of cell No. 2. This heat balance formula shows the importance of decreasing the temperature of cell No. 2 ($T_2$) which would have a significant impact on decreasing the heat output back to pre-thermal runaway.

### 9.3.1 Water-Based Systems

One of the oldest firefighting agents, water-based fire systems have proven to be a very effective at both suppression and extinguishment of fires. Water is abundant and with its high latent heat of vaporization and heat capacity makes it an ideal firefighting agent. However, when regarding LIB hazards certain installation criteria should be considered, such as electrical conductivity dangers, fire seat penetration, reactivity to water, significant water supply, and excess water management. Water is a conductive medium that when used on an electrical equipment can introduce additional risks to the incident such as electrocution, short-circuiting, and damage to equipment [45]. Indiscriminate applications of water on an electrical hazard like an LIB would thus be inappropriate and likely cause additional problems. To effectively use water as a firefighting agent it needs to reach the seat of the fire which is another issue when dealing with LIB installations. LIB cells are generally surrounded by protective layers and even IP-rated enclosures to protect the LIB cells during normal operating conditions. This shield of armor makes penetrating to the seat of the fire difficult if not nearly impossible. To make up for the inaccessibility to the LIB cells and seat of the fire, the solution is to supply excess amounts of water to both cool the exterior of the LIB and give the best chance of getting water to the failed LIB cell(s). This excessive amount of water needed to respond to an LIB fire means consideration needs to be made for a properly sized water supply and disposal of used firefighting water. To improve the effectiveness of water-based fire protection systems, it is thus recommended to have the system installed inside the LIB module, pack, and/or rack to have a more effective distribution and heat dissipation capabilities [69]. In testing comparing local application of water spray to the exterior of an LIB pack and internal injection of water [203], the external tests required >1000 L of water while the internal tests required only 13 L. When water does interact with the combusting LIB cell a secondary effect to the heat dissipation is the formation of HF [61]. In fire tests done by Larsson et al. [92,204] concluded that applying water to an involved LIB increased the peak HF production rate, some cases by up to 35%, but did not however change the total amount of HF produced. This increased production rate might be a concern for evacuation tenability criteria during activation of water-based suppression and extinguishing systems.

A thorough review different application methods of water-based fire protection systems for LIB hazards done by Ghiji [111] identified water jet, water sprinkler, and water mist systems. A water jet applies a directed stream of water to the target hazard. This is generally done manually by firefighters running handlines to the fire, but it also can be found as fixed fire firefighting systems that can be set to target the base of the fire remotely or automatically. A water sprinkler projects a spray of water droplets with enough momentum to penetrate the fire plume which directly cools the surrounding surfaces and when the droplets vaporize cools the air. A water mist system projects a very fine distribution of water droplets, less than 1000 µm in diameter, with a larger surface area to volume ratio. This ratio results in improved heat absorption capabilities. The capabilities of water mist systems that makes it more effective for an LIB fire [205] are (1) gas-phase cooling, (2) oxygen depletion and flammable vapor dilution, (3) wetting and cooling of the fuel surface, (4) radiation attenuation, and (5) kinetic effects, enclosure effects, turbulent mixing, and cycling. Improved gas-phase cooling for water-mist system is accomplished by the vaporized fine water droplets absorbing heat within the combustion zone to decrease the temperature of the flame and if applied correctly reduce the flame temperature to the critical extinction temperature.

Water has significant volumetric expansion when vaporized which causes a disruption of air entrainment to flame and a cascading impact on concentrations of oxygen and combustion gases around the flame. Within an enclosure, the oxygen concentration decrease depends on the size of the enclosure and fire, ventilation conditions, and length of the pre-suppression period. Depending on these conditions the oxygen concentration can decrease from a combination of displacement from water vapor, fire consuming limited oxygen supply, and dilution from fire gases [206].

The very fine water droplets from a water mist system come as a distribution of droplet sizes so larger droplets with sufficient momentum, like the water sprinkler, can penetrate the fire plume to wet and cool the fuel surface causing a reduction of the fuel pyrolysis rate [111].

An interesting effect the water mist system takes great advantage of is radiation attenuation caused by the injection of water vapor between the flame and fuel. A comparison between water mist systems with different droplet sizes [208], identified that finer droplets will attenuate radiation at a lower concentration of water. The radiant energy released by the flame is absorbed by the water vapor which decreases the radiant heat flux to the walls of an enclosure [205] and heat re-radiating back to the fuel surface [209]. An experimental study by Mawhinney et al. [205] found that when using a water mist system, the radiant heat flux to the enclosure walls can be reduced by 70%.

The kinetic effects of a water mist system are interesting because they can both intensify and extinguish a flame. Mawhinney et al. [210] noted that water mist systems can intensifying a flame due to increased turbulence and entrainment caused by vaporization at the flame surface. Increased turbulence and entrainment can further improve flame characteristics like increased fuel/air mixing rate and combustion rate. Alternatively, the kinetic effects of a water mist system can extinguish a flame in combination with flame cooling (gas-phase cooling) by diluting the combustion gases and distance the combustion rate far enough from the stoichiometric condition to lead to flame extinction.

Experimental studies on enclosure effects of a water mist system [205,211] has shown that installations in enclosures have intensified oxygen depletion and dilution influence, a water mist system will quickly cool a heated upper layer, localized oxygen depletion caused by the momentum of expanding water vapor traveling toward fire, and possible volume contraction or negative pressures caused by the rapid cooling of a heated upper layer. Liu et al. [211] has proposed to have stages of water mist activation to gradually build up to the designed discharge rate to limit the kinetic and enclosure effects.

### 9.3.2 Water-Additive-Based Agents

Water-based fire protection systems have proven effective suppression and extinguishing methods for LIB fire hazards, but certain additives may further improve the fire protection systems effectiveness. Common additives used for fire protection systems is firefighting foam, F-500 Encapsulating Agent (EA), Wetting Agents (WA), and Aqueous Vermiculite Dispersion (AVD) agent.

**Firefighting Foam**

Firefighting foam is offered in several chemistries but comes as either a pre-mixed product or concentrate that needs to be mixed with water at a manufacturer defined ratio. Firefighting foam is intended to be used on common combustible (class A) and liquid (class B) fires and is also capable to be applied to LIB fires as well [212]. The working principle of firefighting foam is to cool and seal the surface of the fuel to put a physical barrier between the flammable vapor/oxygen and hot fuel surface. The challenges when applying firefighting foam to LIB fires is completely encapsulating the LIB cell, multi-stage jet fires breaking the foam surface, and internal oxygen generation from cathode decomposition [111].

**F-500 Encapsulating Agent (EA)**

A newer water additive for fire protection systems is the F-500 encapsulating agent (F-500 EA) manufactured by HTC which has been tested and approved for common combustibles (class A), liquid (class B), metal (class D), animal fats (class K), and LIB fires. HTC provides suggested operating guidelines for the mixture ratio of agent and water for ideal performance. The unique capabilities of F-500 EA are an increased heat capacity 6-10 times than water, encapsulation of fuel in Spherical Micelles (A.K.A. chemical cocoons), and interruption of free radical chain reaction. These capabilities result in improved fire suppression or extinction and reduced generation of smoke, soot, and toxic gases. The encapsulation capability functions at the molecular level which makes F-500 EA a perfect solution for three-dimensional fires as compared to firefighting foam. F-500 EA is environmentally safe, particularly compared to firefighting foam, because it is non-hazardous, 100% biodegradable, and contains no fluorinates ingredients. Fire testing by Luo et al. [213], compared pure water mist systems with a water system mixed with 5% of F-500 EA to measure difference in extinguishment time and quantities of agent required for extinguishing. The difference in performance was dramatic with the water system mixed with 5% of F-500 EA extinguishing the LIB fire so quickly that it was difficult to measure the little amount of water used. Additionally, the F-500 EA system prevented reignition of the LIB.

**Aqueous Vermiculite Dispersion**

Aqueous vermiculite dispersions (AVD) is a premixed aqueous solution of exfoliated vermiculite that when dispersed over a flaming surface will both cool the fire and form a physical oxygen barrier. The cooling effect comes from both the water in the solution and the chemically bound water within the vermiculite. The oxygen barrier is nonflammable and is formed when the vermiculite platelets dry on the fuel surface and bind together. Benefits of AVD identified by Fire industry Association (FIA) [200] for response to LIB fires are the immediate cooling effect of the water, physical oxygen barrier, vermiculite is not electrically conductive, effective as a thermal runaway propagation inhibitor, easy to deploy, and environmentally friendly. However, fire testing using this agent show less than adequate results. Andersson et al.[69] tested use of AVD in a series of test to compare fire protection systems. They found that AVD can extinguish an LIB fire although, likely due to its high viscosity, cannot quickly penetrate deep into the LIB to cover the compromised LIB cell. Thus, limiting the effectiveness of AVD as an LIB fire extinguisher.

**Wetting Agents**

A wetting agent (WA) are defined by FIA [200] as liquid concentrates which, when added to plain water in proper quantities, materially reduce the surface tension of plain water and increases its penetration and spreading ability. When applied to LIB fire hazards the wetting agent can help to increase the cooling rate of plain water and in turn reduce the amount of water considered for both supply and post-event clean up. Zhu et al. [214] has shown significant performance improvements of water mist systems and also noted a decrease in $CH_4$ and CO production. This may be due to quicker cooling rates or chemical bonding of the surfactants to $CH_4$ and CO.

### 9.3.3 Gaseous and Aerosol Systems

These systems inject or produce gases to suppress and extinguish fire development. In a gaseous system, the agent is stored as a pressurized multi-phase liquid, commonly one or a combination of nitrogen, argon, carbon dioxide, that is injected into an enclosure to dilute the oxygen concentration. There are little cooling effects from these systems, but they have been shown to be effective for lowering the risk of thermal propagation within the LIB [215]. Since LIB fires can self-generate oxygen, the gaseous systems oxygen depletion capabilities would need to be significant enough to extinguish the flames [200]. The other concern with this system is that since there is no cooling effect the internal reactions within the failed LIB cells can continue and excess fire gases will be generated. This would only move the problem from post to pillar.

In an aerosol system, the agent is stored as a solid compound within a non-pressurized container, sometimes called a generator [200]. When the system is activated, the solid compound begins to decompose and floods the enclosure with the agent. The reacted agent acts as a chemical inhibitor for flaming combustion and is intended to extinguish the fire.

When applied to LIB fires, chemical inhibition without any cooling effects has a similar result as a gaseous system with increased fire gas production. Due to the way LIB fires develop, aerosol and gaseous systems may not be effective on their own. However, if these systems can be combined with a means of cooling, then they may prove to be part of an effective solution [215].

### 9.3.4 Clean Agents

NFPA 2001 [216] defines clean agents as a volatile or gaseous fire extinguishant that is electrically nonconducting and that does not leave a residue upon evaporation. An early well know example of a clean agent is halon. Halon has been around since the 1960's and functioned as an incredibly effective fire extinguishing agent that has been an integral fire protection system for state-of-the-art installations like naval vessels, nuclear power plants, aircrafts, submarines, etc. Later it has been discovered that this agent is incredibly damaging to our environment and namely ozone layer and all halon production has been discontinued. Similar products have since been introduced and their effectiveness has been tested for LIB fires.

A popular clean agent used today is heptafluoropropane (FM-200), which does not lead to ozone depletion and from testing done by Wang et al. [217] and Rao et al. [218] has shown superior fire suppression capabilities. Another popular clean agent is Novec 1230 which has seemed to have a slightly improved performance, identified by the reduced concentration of Novec 1230 required for flame extinguishment [216]. Additionally, it has been noted that Novec 1230 has a longer hold time than FM-200 and can have an effect of decreasing the CO concentration within an enclosure [96]. LIB fire testing conducted by Liu et al. [219] showed Novec 1230 to be just as effective at suppressing the LIB fire as FM-200. A newer clean agent introduced by Wang et al. [219,220] called C 6 F-ketone has been tested on LIB fires and shown to be another candidate for suppressing and extinguishing LIB fires. The shared issue with the identified clean agents is the reduced or lack of cooling effects to the LIB fire and it has even been proposed to use clean agents in conjunction with a water-based system to achieve better results [96]. The need for cooling capabilities while using a clean agent system is highlighted by the thoroughly investigated McMicken LIB ESS explosion in Surprise, Arizona [116,221–223], a very good case study on the hazards associated with LIB ESSs. The LIB ESS that exploded was equipped with a stand-alone detection system, control system, and a Novec 1230 fire protection system. During the early fire development stage of the LIB fire, the Novec system was discharged and possibly did extinguish the fire. However, due to LIB's internal heat generation capabilities after thermal runaway the LIB continued to decompose and notoriously resulted in an explosion severely injuring four of the firefighters attempting entry into the LIB ESS structure.

### 9.3.5 Carbon Dioxide Systems

A popular firefighting agent used in many industries, carbon dioxide systems have proven to be highly effective at fire suppression and extinguishment. However, when applied to LIB fires the quality of performance is lacking. A CO2 system functions by either filling an enclosure or locally applying gaseous CO2 to a concentration that will displace enough oxygen to extinguish flaming combustion. When dealing with LIB fires, cooling of the cells is mission critical, and a CO2 system is just not designed to cool down an LIB. Work done by Wang et al. [220] has concluded that a CO2 system on its own would not be an effective fire protection system for an LIB hazard.

### 9.3.6 Chemical Powder Agents

The working principle of chemical powders is to act as a chemical inhibitor for flaming combustion when dispersed into the flame plume and on the fuel surface. The powder has no cooling effects and for fires with high fuel surface temperature, such as LIB fires, provide no functional oxygen barrier [45]. The lack of cooling effect is not surprising since there is no bounded water to these powders but the inability to form an oxygen barrier is due to the relatively low decomposition temperature (i.e. ABC and BC powder decomposes at 193.5 C and 106.0 C, respectively) [96]. Since a when an LIB cell fails the surface temperature is already approaching 200 C, application of chemical powders would be ineffective. In addition to being ineffective for LIB fires, application of chemical powders within an occupied enclosure can create inhalation risks and potential breathing problems [224].

## 9.4 Manual Operation Considerations

When a fire develops that is beyond than the capabilities of the fixed fire control systems then manual fire operations are required. These operations involve highly trained personnel to respond to hazardous scenarios with the consideration of life, property, and the environment. When responding to an LIB fire event there are additional risks associated such as increased toxic gas production, explosions, projectiles, jet flames, and spontaneous re-ignition. This section is intended to review the existing tools available for the CERN fire and rescue service (CFRS) and similar underground facility fire departments.

### 9.4.1 Pre-incident Management

The information of a fire incident provided to the responding CFRS is limited due to several factors such as the evolution of the fire since being reported, broken lines of communication, miscommunication by the on-scene observer, and physical obstruction of the fire source. To compensate for these understandable sources of misinformation, the CFRS are trained regularly to adapt to changing fire scenes. The wide variety of risks and hazards of an LIB have been addressed in previous sections and it is expected that a responding fire crew can appropriately handle an LIB fire hazard. The issue is identifying that it is an LIB while responding. To assist with this task, clear identifying marks should be placed on all LIB devices and the CFRS should be trained to identify these markings as an LIB hazard. Once the fire is identified as an LIB fire, power should be safely disconnected based prior to beginning firefighting operations based on site specific guidelines. Examples of appropriate guidelines are the SAE International guide [225], CTIF [226], and the NFPA EV Emergency Response

Guides [227]. Sun et al. [43,44] reviewed different codes, procedures, and guides from different countries to provide a recommended EV firefighting process. This has been adapted and applied to general LIB installations:

1) Identify that the fire is an LIB fire and if available refer to the correct rescue (for EV) or response procedure.
2) Determine the firefighting plan based on the situation.
3) Protect the people first.
4) Control or extinguish the fire, and if the LIB is charging, switch off the charging infrastructure if possible.
5) If the LIB is not stationary it should not be moved immediately, after the fire is extinguished.
6) Monitor the LIB and surrounding area for changes in temperature and gas concentrations.
7) The final step is on-site cleaning.
    a. Disposal procedures are recommended for removing used fire extinguishing agents
    b. if the LIB is not stationary; it should be moved to an outdoor place after the accident because of risk of reignition.

### 9.4.2 Personal Protective Equipment

A literature review completed by MSB [228] recognized that LIB fire incidents within enclosed spaces such as parking, garages, tunnels, and buildings pose a difficulty on reaching the fire due to the significant production to smoke and fire gases. MSB also recognized the risk of increased HF production and the multiple routes of exposure: inhalation, dermal, and mucous membrane exposure. Nordström [229] also noted that most serous near-accidents for firefighters occur in underground parking garages due to the large quantities of dense smoke and fire gases. Due to these exposure risks and penitential for extended exposure during fire operations, appropriate levels of PPE should be considered. Välisalo [230] reviewed the conventional personal protective equipment (PPE) used by firefighters, full turnout gear and self-contained breathing apparatus (SCBA), when responding to an LIB fire. It was determined that even with the higher concentration of HF the conventional PPE was effective enough to limit exposure but recommended using PPE with a higher water vapor resistance such as level Z143. Välisalo [230] also considered the risk of shock and electrocution during firefighting operations against an LIB fire. It was determined that use of conductive firefighting agents, such as water, do not increase the risk of shock or electrocution but recommended to not directly touch the compromised LIB without the use of electrical PPE. As for the risk exposure to the personnel, the working personnel at CERN have access to personal breathing apparatus to assist with evacuation but the effectiveness against HF is not know currently.

### 9.4.3 Cooling Methods

Once an LIB fails and results in a fire the first objective of the responding fire crew should be to cool the LIB to reduce the temperature of the failed LIB cell and surrounding cells and environment [226]. Ghiji et al. [111] reviewed LIB fire suppression options and concluded that cooling the LIB is even more important than extinguishing any flaming combustion. This priority is meant to prevent thermal propagation to non-compromised cells in the failed LIB. MSB [228] fire tests showed that extinguishing agents with good heat capacity are best for responding to an LIB fire. As such, the preferred agent used was water which if applied directly to the LIB at a low water flow for a longer period had a good effect in cooling the LIB.  Ghiji et al. [231] reviewed experimental studies completed by the Fire Protection Research Foundation (FPRF) [102], Federal Aviation Administration (FAA) [232], and Det Norske Veritas and Germanischer Lloyd (DNVGL) which also concluded that the most effective firefighting agent to use on LIB fires are water-based agents. The Federal Aviation Administration (FAA) [232] found that water-based agents are much better than non-aqueous agents due to the difference in cooling capabilities. To improve the effectiveness of water as a firefighting agent, additives can be mixed with the water. Egelhaaf et al. [233] tested water with additives, such as surfactants and gelling agents, to see their impact on suppressing an LIB fire. It was concluded that these additives are effective and in turn reduce the total amount of agent required.

A significant issue when externally cooling an LIB is that access to the compromised cells is blocked by protective enclosure surrounding the LIB. The protective enclosure is needed to limit sources of external abuse but this in turn hampers firefighting operations in the event of a fire [228]. This inaccessibility of the LIB during a fire incident has been shown to require an increased in the amount of firefighting agent [234]. To get firefighting agent into the LIB it is recommended to utilize cooling channels if they exist or to install fire connection ports for manual injection of the agent [230]. If the agent can get directly into the LIB to cool the cells the cooling effect will be greatly increased, and the minimum amount of agent would decrease.

A novel concept to reduce exposure times for firefighters is the use of portable water mist systems as proposed in the ALBERO project [235]. The working principle of this technology are portable ground applicators (a stainless-steel pipe with specifically oriented water mist nozzles on it) that project a curtain of water at and around an LIB fire. This system has been proven effective with protecting the surrounding fuels but not 100% effective in extinguishing the involved LIB. The use of water-mist nozzles would help to reduce the amount of water discharged during firefighting operations when compared to traditional hose lines but still introduces a secondary hazard of polluted wastewater.

### 9.4.4 Smothering Methods

A more passive firefighting operation when responding to an LIB fire is to smother the LIB fire to prevent fire spread to surrounding fuels and excessive heat exposure to the tunnel structure. The act of smothering an LIB fire is to form an oxygen barrier to stop flaming combustion, like fire suppression. This fire response method, however, does not stop thermal propagation between the LIB cells due to internal exothermic chemical reactions and oxygen generation caused by the decomposition of the cathode. Therefore, smothering an LIB fire will likely result in total consumption of the LIB until all active material is spent.

Some smothering methods tested on LIB fires are AVD, LIB fire blankets, and LIB fire containers. The AVD can be stored within portable fire extinguishers and be manually dispersed over an LIB fire to form and solid oxygen barrier over the LIB. The working principle of AVD is detailed in section 9.3.2. The other smothering methods for LIB fires are the LIB fire blanket and container which function by physically surrounding an LIB to suppress flaming combustion. Two manufacturers of LIB fire blankets are Bridgehill based in Norway and AVD based in the UK offers an LIB fire blanket designed for covering burning EVs with dimensions of roughly 6 m x 9 m. Archived tests using these blankets show implementing the blankets on outdoor parking lots. Concerns with use of this method of smothering are the limited space in tunnel applications, excessive production of smoke and fire gases generated from inefficient combustion of the LIB, and proximity exposure risks to the responding firefighter. The LIB fire container is a product of AVD that is built of the same material as the fire blanket. The intention of this product is to place smaller portable LIB hazards within to be moved outdoors and allow to continue to burn until all active material is spent. This method of smothering shares the same concerns at the fire blanket. To best use these smothering methods for handling LIB fires an adequate fire gas handling system should be installed to ventilate the tunnel both during and after application of these methods.

### 9.4.5 Post-incident Management

After an LIB fire has been extinguished, additional steps should be taken to get the facility back and running: (1) unburnt combustion gases vented from the LIB and neighboring fuels need to be handled appropriately, (2) used fire extinguishing agents need to be collected and disposed of correctly, (3) the temperature and gas concentrations around the extinguished LIB needs to be monitored to prevent reignition, and (4) surrounding equipment that may have been damaged during fire operations need to be inspected for potential fire risks.

# PART IV – LIB Recommendations, Research Gaps, and Conclusion

# 10. Recommended Fire Safety Considerations for Lithium-ion Battery Technologies in Tunnels

Unfortunately, there is no universal solution for LIB fires and each application should be reviewed on a case-by-case basis. The general LIB fire detection and response methods have been addressed in sections 8 & 9 respectively but when implementing within CERN tunnels a more idealized solution can be offered. This section provided key recommendations for these technologies within CERN tunnels. A common trend for these recommendations is built around time. Shortening the time for fire detection, response, extinguishment, and post-incident while lengthening the time for onset of thermal runaway, thermal propagation, and duration of protected coverage.

## 10.1 Improved Early Detection Methods

Due to the decomposition evolution for LIBs, certain criteria for fire detection should be considered: (1) use detection equipment optimized for installation specific LIB chemistry and capacity, (2) identify the ideal mounting location for the selected detection technology, and (3) improve early identification of LIB hazards both before, during, and after a fire incident.

### 10.1.1 Optimized Detection Technologies

LIB applications within tunnels that have entered thermal runaway poses additional risks regarding fire development and toxic exposures. However, if an LIB is monitored so that the stages approaching thermal runaway can be detected the risk of an LIB fire may be reduced or even prevented. Due to the internal electrochemical reactions an LIB cell experiences approaching thermal runaway, an amount of gas is vented as the internal pressure increases within the cell in a process called off-gassing. It is therefore proposed that monitoring for this off-gassing event using gas sensors could be provide a more sensitive and accurate measurement of an LIB cell approaching thermal runaway [236]. An experimental study completed by Koch et al. [237], compared the ability between voltage, temperature, gas, smoke, pressure, and creep distance sensors for detecting a thermal runaway event. They concluded that regardless of the abuse source, the highly sensitive gas sensor was the best option and if implemented correctly could identify early stages preceding a thermal runaway event. Types of gas sensors which show promise based on experimental testing are the Figaro TGH822TF gas sensors [238] and a custom $SnO_2$-based ceramic semiconductor gas sensor [239]. The gases sensed by the Figaro sensors are hydrogen and carbon dioxide gases while the latter sensor monitors electrolyte vapors, volatile electrolyte solvent, and volatile components of an electrolyte mixture of the battery. These gas sensors work best when installed at the LIB module, pack, or rack level due to proximity to the LIB cell but does not work as a full enclosure detection option.

If gas sensors cannot be placed within the LIB to monitor the cells, then a full enclosure detection option should be considered. Detection options at this level is not likely to detect early-stage thermal runaway event so post thermal runaway conditions should be considered. After an LIB cell experiences thermal runaway significant quantities of smoke and gases are produced and likely followed by a fire or explosion. Based on the detection options addressed in section 8, the best detection technology at the enclosure level would be smoke detectors. Of the addressed smoke detection options, active air sampling provides the greatest level of sensitivity and accuracy and would thus be the best option for monitoring for LIB fires. These detectors provide an additional level of accuracy by including monitoring for certain gas species such as hydrogen, carbon monoxide, and hydrocarbon gas which are vented during an LIB experiencing thermal runaway. If no prompt response is taken after detection sends an alarm signal, the thermal runaway event can continue to evolve and develop a serious fire or explosion hazard. Thus, after an alarm signal is sent, actions should immediately be taken to disconnect the compromised LIB module(s) and activate response protocols [138].

### 10.1.2 Idealized Detection Mounting Location

As with most detectors, closing the distance between detectors and the hazard improve the detection time of a failure event. When considering LIB hazards, the LIB is enclosed within a protective enclosure that can delay the release of smoke and fire gas into the enclosure. Therefore, the ideal location to install detection technologies is within the LIB. If it is not possible to place detection devices within the LIB then critical monitoring points should be focused on. A general detection network would be present throughout the tunnel however the highest probability of an LIB fire occurring is during charging. Therefore, charging locations for LIB devices and EVs should be closely monitored for an LIB undergoing thermal runaway.

### 10.1.3 Improved Identification of LIB Hazards

Since the range of applications for LIBs are expanding so quickly, it may not be obvious that the equipment is powered by an LIB. This obscurity can lead to misinformation when reporting a fire incident and delays in appropriate fire response. To overcome this challenge, clear identification markers/placards should be placed on LIB devices and installations. These markers/placards could be like the UN3840 label and installed in a highly visible place. Working personnel and of course CFRS should be trained to recognize this newer hazard and, if applicable to their position, learn to recognize early signs of a thermal runaway event.

## 10.2 Improved LIB Fire Safe Designs

The inherent dangers of LIBs are many, but steps can be made to improve the level of fire safety within their design.

### 10.2.1 Consideration of capacity for LIB systems

A factor important to impacting the severity of an LIB fire is the capacity. AN LIB with an increased capacity increases the HRR, PHRR, and radiative heat flux while decreasing the onset time for thermal runaway. Due to these concerns when dealing with higher capacity LIBs certain limitations should be set by the installation facility. For instance, when implementing a stationary LIB ESS, it would be recommended to divide the total energy demand over multiple isolated and protected ESSs (i.e. if 2 MW of power is needed, it could be supplied by ten separate 200 kW LIB ESSs). This limitation of capacity may however be an issue when dealing with LIB pack within EV powertrains which cannot be further compartmentalized. EV powertrains come within a range of power supplies from 20 – 100 kW which increase when considering heavy-duty EVs like mining vehicles. To compensate for this range of capacities, it would be recommended to limit operation of portable LIBs within protected areas. These areas would be designed to detect and respond to an LIB fire hazard based on the specified LIB capacity limit. For instance, at CERN, a tunnel section may be divided into certain protection areas such as:

Zone 0: Stationary LIB ESS
Zone 1: Charging station for lightweight EVs
Zone 2: Lightweight EV travel accommodations (E-bikes, scooters, golf carts, etc.)
Zone 3: Active worksites using LIB powered tools
Zone 4: Charging station for portable LIB devices

This is an arbitrary division of zones of LIB fire safety, a thorough investigation by the installation facility should be done. The goal of the investigation to define both the capacities of LIBs within the zones and adequate response capabilities to handle an LIB fire of similar capacities.

### 10.2.2 Access port for fire protection system

As previously addressed, the LIB is by design well protected within an enclosure, often a watertight IP-rated enclosure. This enclosure is counterintuitive when trying to access and cool the compromised cells within the LIB. This is a concern shared by international fire departments in response to difficulties in extinguishing EV fires. A typical EV fire scenario operation time tends to be much longer than an ICEV fire and the amount of firefighting agent used is significantly more as well. In these fire scenarios, the fire occurs outdoors and both time and water are not a limiting factor. When introducing the same fire scenario to a tunnel hazard, the problem becomes much more complex. To assist with reducing the amount of time responding to an EV fire and the amount of agent required, a fixed access port could be installed on the exterior of the LIB. This access port would provide direct access to the LIB and compromised cells in the event of a thermal runaway. This would mean immediate, direct cooling to the compromised cells are possible immediately when a thermal event is detected.

### 10.2.3 Consideration of LIB chemistry and SOC

When considering the type of LIB to install or introduce to a tunnel like CERN, the LIB chemistry and SOC should be deliberated. Of the variety of LIB chemistries, the LFP LIB has shown the greatest thermal stability with a slight reduction in internal capacity and performance. However, this reduction in performance (3.6V LFP cell compared to 4.2V cell in other chemistries) means an increase in the total number of cells required to match the power requirement of the LIB application. The SOC is another factor that affects the LIB fire severity and sensitivity to entering thermal runaway. A higher SOC (approaching 100% SOC) increases likelihood of an LIB fire and often increases the severity of the fire. Of the LIB chemistries, LFP cells have significantly reduced fire severity at 75% SOC and lower. However, to keep an LIB installation at or below 75% SOC would mean increased operational costs because a greater number of cells would be needed in the LIB installation. A cost benefit analysis would be needed to decide how to proceed.

### 10.2.4 Improved BMS and TMS

The BMS and TMS are mission critical aspects of safely operating LIBs. The working principles of the BMS and TMS are detailed within section 8.2.3 and 9.2.1 respectively. These systems keep the LIB within the safety window of appropriate voltage and temperature limits. Exceeding these limits can send an LIB into thermal runaway and if left unchecked result in a fire or explosion. The BMS can be improved by increasing the number and sensitivity of internal sensors while the TMS can be improved by increasing the cooling factor of the chosen method of cooling. Without built in redundancies an LIB fire may still occur.

### 10.2.5 Considerations for Surrounding Area Design

Wherever an LIB is planned to be implemented at CERN, designs for an LIB fire and explosion should be considered. The considerations for the area around an LIB application are ventilation sizing to handle the smoke and vented gases, evacuation concerns for working personnel, ignition sources within LIB areas, and explosion risks for surrounding equipment and structural members.

### 10.2.6 Real-time display of LIB status from the BMS

A real-time display of LIB status and ambient conditions outside of LIB area is recommended. Ideal LIB criteria to display would be LIB temperature, voltage, and SOC while the ambient criteria would be temperature, O2 concentration, and other gas concentrations (i.e., CO2, CO, H2, hydrocarbons, etc.). This display would assist with both maintenance and CFRS response while reducing exposure risks.

## 10.3 Prompt Fire Response Strategies

After an LIB has entered thermal runaway, prompt response is important to limit the number of cells involved. There are many response options detailed in section 9 of this report, but this section provides recommendations specific for application at CERN.

### 10.3.1 Recommended firefighting agent

When choosing a firefighting agent for handling an LIB fire, the cooling factor of the agent is of greatest importance. Between cooling and extinguishment of the fire, it has been shown that cooling of the LIB takes priority. In review of the cooling capabilities of available firefighting agents, water-based agents provide the greatest cooling factor. However, the repeated challenge of access to the LIB cells during fire responses is yet again a problem that needs addressing. The use of additives mixed with water helps to penetrate the LIB by reducing water surface tension and directly cool the compromised LIB cell(s). Additional additives like F-500EA, can be used to inhibits chemical chain reactions of the vented gas to improve both cooling and fire extinguishing capabilities. There are numerous aqueous solutions on the market that show promising as a firefighting agent for LIB fires, but a thorough review needs to be completed.

### 10.3.2 Fixed fire protection systems

Due to the potential secondary risk to surrounding equipment, a fixed fire protection system is a rare find within CERN underground installations. However, a fixed fire protection systems can be a safe and effective fire protection option. As with most aspects of fire safety with LIBs, the ideal location of implementation is as close as reasonably possible to the LIB cells. A fixed fire protection system integrated at the LIB pack and rack level is possible and proven very effective during fire testing. Installing a system at this level provides direct application of the chosen firefighting agent to the LIB modules. If interconnected with a detection and control system, the whole operation can be done intuitively without delay of application. This integrated method of using a fixed fire protection system would limit the fire development, amount of agent required, and increase response times. This type of fire protection system is applicable for larger capacity LIB applications, but smaller LIB applications would demand an enclosure level fire protection system. To protect these smaller LIB applications (lightweight EVs, tool packs, portable devices, etc.) a water mist system has shown to provide the best protection capabilities while limiting damage to surrounding equipment.

### 10.3.3 Manual fire protection tactics

When a fixed fire protection system is not viable or not fully effective at extinguishing an LIB fire, manual fire operations are required. Regarding CERN, the CFRS is prepared to respond to all fire events promptly and prepared but there currently is not a specific protocol for dealing with an LIB fire. It is recommended that a protocol be generated for each LIB application within the tunnel network to provide the best approach in extinguishing the fire. This protocol would also include stages of response from working personnel evacuation to post incident management.

### 10.3.4 Safety concerns for working personnel during evacuation

As identified, LIB fires produce a significant amount of smoke and toxic gases. Of particular concern is HF which has several routes of exposure (inhalation, dermal, and mucous membrane exposure routes). Working personnel have access to personal filters to wear if evacuating through dangerous environments however it is not clear if this is adequate for a high HF environment. Due to his concern, it may be recommended to continue or increase mechanical ventilation of the affected tunnel(s) during evacuation.

### 10.3.5 Post-incident management

After an LIB fire incident, there will be additional steps necessary to get the facility back and running. The key steps of post-incident that should be addressed are:

1. Removal of all unburnt combustion gases from the tunnel
2. Used firefighting agent shall be collected and disposed of correctly
3. The LIB and area around the extinguished LIB should be monitored for changes in temperature and gas concentrations.
4. The surrounding equipment should be inspected for fire risks and damage caused by the fire or during fire operations.

Generation of a post-incident protocol is recommended to shorten shutdown times and limit cost to the operation.

# 11. Research Gaps for Responding to Lithium-ion Battery Fires

Great steps have been taken to improve fire safety of LIB applications but as LIB technology continues to evolve the gap of fire safety and performance continues to increase. Current research gaps noted for handling LIBs are:

- Environmental impact of used water after firefighting operations
- Impacts of underground effects on LIB fire development
- Investigate the impact different spacings, such as gaps between LIB modules and racks, has on thermal propagation
- Impact firefighting operations has on vented LIB gas generation
- Correlation between LIB installation capacity and gas generation
- Conflicting LIB codes and standards
- Scalability of bench-scale testing to full scale fire testing
- Standardization of LIB fire and abuse testing at to better quantify safety of LIBs

# 12. Conclusion

LIB offers an effective, modern solution for lightweight battery energy storage due to its high voltage capacity, longer lifespan, decent energy density, and low self-discharge. However, the increase in performance also presents unique fire hazards relative to other battery energy storage (i.e. NiCd, VRLA, REDOX, Flow, etc.). The concern for safety of an LIB is when the LIB is operating outside of the safe operating window within the limits of voltage and temperature. Outside of this safe operating window an LIB can experience a thermal runaway event. This event can occur due to an abuse condition (thermal, mechanical, and electrical abuse) and result in generation of heat, vented gases and volatiles, fire, and explosion. The severity of these results can be limited based on the LIB chemistry, safety devices, capacity, cell arrangement, and SOC.

There are six common LIB chemistries used today (LFP, NMC, NCA, LMO, LCO, and LTO) which each provide varied performance criteria and fire safety. Of the current chemistries, the LFP cell provides the greatest thermal stability with a decrease in sensitivity to abuse sources and severity of fire events. Additives and modifications within the LIB cell, electrolyte additives, electrode modifications, shutdown separators, etc.) provide increased fire safety but can have negative impacts on the LIB performance and life span. The LIB capacity and cell arrangement are other factors affecting the severity of an LIB fire that show reduced capacities and spacing between LIB modules reduce fire severity by limiting cell-to-cell thermal propagation.

Once the best LIB installation is chosen for the operation specific application, monitoring and fire detection is a critical aspect of fire safety. Based on experimental studies on early detection of LIB fires, gas monitoring provides the greatest chance of detecting a failure of the LIB. An incipient stage preceding a thermal runaway event is the venting of gases from the compromised LIB cell to relieve over pressurization in an event termed off-gassing. Gas sensors installed within the LIB can detect the off-gassing event and if interconnected with a control system, TMS, and fire protection system the compromised LIB cell(s) can be prevented from entering thermal runaway. This detection options provides the greatest probability of stopping or limiting LIB an LIB fire but if an integrated detection system is not possible, an enclosure level detection system should be considered. Based on experimental studies on enclosure level detection systems and based on tunnel dynamics, the best detection system at the enclosure level is a smoke detection system. Of the variety of smoke detectors, an active air sampling system, possibly combined with a gas monitor, provides the highest accuracy and quickest detection time for an LIB fire.

Once an LIB is compromised and enters thermal runaway the primary response criteria is to cool the LIB to limit cell-to-cell thermal propagation. Cooling even precedes the need of flame extinguishment due to the internal exothermic reaction within the compromised LIB cells. Therefore, an ideal firefighting agent needs to have a high cooling capacity. Of the available firefighting agents, the agent with the greatest cooling capacity has been shown to be water-based agents, namely water with additives. The trouble with cooling the compromised LIB cell(s) is the difficulty of applying the agent directly onto the cell(s) due to the IP-rated enclosure protecting the LIB from external sources of abuse. As with the detection systems, the ideal installation location for a fixed fire protection system is within the LIB. This integrated fire protection model has been shown to significantly increase cooling rates, decrease the amount of agent required to extinguish an LIB fire, and decrease the quantity of generated smoke and vented gases. If a fixed system is not possible for the LIB application such as lightweight EVs, an enclosure level fire protection system should be considered. An enclosure level fixed fire protection system poses risks to surrounding equipment, a significant concern for CERN, but if appropriately installed the risks can be significantly reduced. Based on fire testing of LIBs, the best fixed fire protection system at the enclosure level is a water mist system. The benefits of a water mist system when combating an LIB fire (detailed in section 9.3.1) are the improved cooling of fire plume, fuel surface, and cells due to the distribution of water droplet sizes that can penetrate deeper into the LIB fire. The finer distribution of water droplets also limit damage to surrounding electrical equipment but should still be a consideration during installation.

When fixed fire protection options are not possible, manual firefighting operations should be considered when generating a fire response plan. When forming response plans for CERN tunnel installations, aspects that should be considered are CFRS transport and travel times, evacuation stages, LIB application specific response, and post-incident management. Due to the vast size of the CERN facility, the time between detection of a fire to arrival of CFRS can be as long as 20 minutes. This implies that an LIB fire without a fixed fire protection system the LIB fire can be allowed to develop into a to a significant scale by the time of CFRS arrival and an appropriate response plan should be formed. To assist with fire response operations by CFRS it is recommended to both define LIB Zones based on the capacity of the LIB application and have application specific response plans for each LIB hazard (i.e., portable devices, tool packs, lightweight EVs, heavy-duty EVs, and LIB ESSs). Based on experimental studies of firefighting operations combating an LIB fire, the best firefighting agent to use is water-based. However, the same concern of the IP-rated enclosure preventing access to the compromised LIB cell(s) remains. Application of firefighting agent directly to the LIB is possible with the addition of a fire connection port on the exterior of the LIB. This connector would allow direct cooling of the compromised LIB cell(s), reducing the amount of required firefighting agent and time of operation. An additional consideration before and during fire response operations should evacuation of working personnel. AN LIB fire produces significant volumes of gases that can hinder egress, so it is recommended that the ventilation system continues to remain operational throughout evacuation. Additional research into ventilation impacts on LIB fire development and impact to firefighting operations should be considered when defining procedures regarding ventilation stages at CERN. After an LIB fire has been extinguished a post-incident management protocol should be generated to address key steps such as removal of all unburnt combustion gases from the tunnel, collection and disposal of used firefighting agent, extended monitoring of LIB and surrounding area for changes in temperature and gas concentrations, and inspection of surrounding equipment for fire risks and damage caused by the fire or during firefighting operations. Whatever method of fire detection and protection chosen by CERN, a fully encapsulating fire response plan completed in cooperation with the CERN fire safety group and CFRS should be generated. This cooperation would greatly increase the level of fire safety at the facility to address this unique fire hazard.

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